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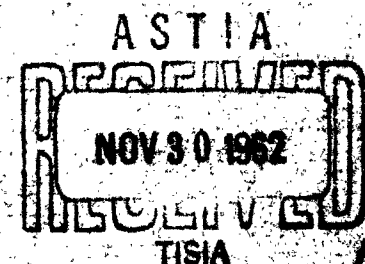
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NOLTR 62-38

NEW ENERGETIC BINDERS FOR SOLID PROPELLANT APPLICATIONS (U)

Prepared by:

B. Burke
H. Heller
J. Hoffsommer
M. Kamlet
R. Rich
M. Stosz

Edited by:

H. Heller

ABSTRACT: A new family of energetic solid propellants based on an energetic binder plus ammonium perchlorate and aluminum is being developed. The binder consists of carboxy-terminated nitropolyesters synthesized from nitroacids and glycerol plasticized by bis(2-fluoro-2,2-dinitroethyl) formal.

These propellants are characterized by excellent thermal stability and insensitivity to impact and shock. Initial extrapolated values of tensile strength and elongation are 4.92 Kg/cm² (70 psi) and 25-30%, respectively. The burning rate at 70.31 Kg/cm² (1000 psi) is 0.914 cm/sec (0.36 in/sec) and the theoretical I_{sp} is 268 seconds.

APPROVED BY: D. C. HORNIG, Chief
Chemical Engineering Division

DONNA PRICE, Acting Chief
Physical Chemistry Division

DARRELL V. SICKMAN, Chief
Organic Chemistry Division

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND

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Work on improved propellant compositions was funded by the Bureau of Naval Weapons as a part of the Advance Fleet Ballistic Missile Studies at the Naval Ordnance Laboratory, Task No. RM 17 30002/212-1/FO09 01 016. This first report covers technical achievements from 1 July 1960 to approximately 1 October 1961.

The investigation was predicated on the assumption that binder systems can be synthesized which will contribute to the thrust of solid composite propellants without sacrificing the level of safety and thermal stability a practical propellant should have. This report presents evidence of the validity of the original assumption. An energetic binder does not, in itself, achieve the future POLARIS aims. It does open up the potential of using fuels and oxidizers which are safer to handle than some test tube curiosities without unacceptable reduction in thrust.

The investigation has benefited and will continue to benefit tremendously from the foundational and applied explosive research programs supported for many years by the Bureau of Naval Weapons. These programs created the unique knowledge on which the present work was based.

Recognition must be given to the contributions of the late Dr. Evan C. Noonan, former Chief of the Physical Chemistry Division at the Naval Ordnance Laboratory. His untimely death prevented his being one of the authors of this report but his influence is there, none the less.

R.E. ODENING

Albert Lightbody
ALBERT LIGHTBODY
By direction

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NEW ENERGETIC BINDERS FOR SOLID PROPELLANT APPLICATIONS (U)

INTRODUCTION AND SUMMARY

This is the initial report on the NOL Polaris propellant formulation program. Its objectives are to develop an insensitive, practical solid propellant in the 260 sec delivered specific impulse range with optimum physical and ballistic properties.

The approach being used to accomplish the above objectives was based on the reasoning that the physical properties of propellants would be improved if the amount of binder could be increased without lowering the specific impulse.

The NOL explosives program has yielded a number of nitro compounds whose chemistry is well known and adaptable to propellant usage. By dissolving an oxidizing plasticizer in and introducing oxidizing groups into the binder it should be possible to produce a propellant requiring a much lower amount of solid oxidizer and possessing a high specific impulse. For safety reasons the matrix itself should not be energetic enough to support a detonation, differentiating this type of composite from those employing double-base binders.

In considering the chemical problems associated with nitropolymers it was decided that the initial approach would be to study carboxy-terminated polyester prepolymers cured with epoxides and plasticized with a high energy nitro-plasticizer. A deliberate attempt was made to select materials which were known to have a high order of chemical and thermal stability. The particular course selected was dictated by materials known to be readily accessible through available intermediates. Initial emphasis was placed on the availability of the material rather than the ultimate in performance.

Two types of polyester prepolymers have been prepared. The first has two reactive carboxy groups and was synthesized from two moles of glycerol, 3 moles of dinitropimelic acid and two moles of either fluorodinitrobutyric acid or dinitrovaleric acid. A second polyester containing three carboxy groups was prepared from three moles of dinitropimelic acid and one mole of glycerol. Bis-fluorodinitro ethyl formal (FEFO) was used as a plasticizer for both prepolymers. These prepolymer solutions are viscous liquids containing about 50% FEFO.

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Polymerization studies were carried out on the nitro-polyester solution prepolymers using various epoxides as crosslinking agents and a dicyclocdiepoxy carboxylate (Epoxide 201) was found to yield a cured binder with the best balance of physical properties. An effective catalyst for the cure reaction was found in a boron trifluoride ethyl ether complex.

The physical properties of the cured binder were studied as a function of catalyst, cure temperature, stoichiometric composition and type of curing agent. A study was made of the batch-to-batch variation of the prepolymer by the determination of the neutralization equivalent of the prepolymer solution and the effect of this variation on the physical properties of the binder. The average molecular weight of the polyester and the acid functionality were calculated and the effect of these values on the physical properties was noted.

The best binder made to date had a maximum tensile strength of 4.71 Kg/cm^2 (67 psi) and an elongation at maximum stress of 104%. Its density was 1.50 gm/cc (0.0542 lbs/in^3) and the thermal stability was $2.66 \text{ cc gas/gm/48 hours}$ at 120°C . The binder was very insensitive to impact having a 50% impact height of 320 cm compared to a TNT value of 150 cm. The cure conditions were 72 hours at 60°C .

Propellant compositions made with nitropolyester binders and containing up to 70% ammonium perchlorate (AP) and aluminum (Al) were easily processed with conventional composite propellant formulating equipment. The pot life and viscosity appeared to be adequate and reasonable although these properties have not been fully determined.

An investigation was started to determine the mechanical properties of a propellant composition containing binder/AP/Al (40/45/15), although later more complete calculations showed that the maximum calculated Isp occurred at a composition of binder/AP/Al (52/28/20). Initial results indicated that the mechanical strength properties of these propellants were low. Subsequent formulation resulted in binders with improved physical properties. Although propellants made with these improved binders have not been tested, previous correlations between binder vs propellant physical properties indicated that these propellants would have tensile strengths of about 5.62 Kg/cm^2 (80 psi) and elongation at maximum stress of 25-30%. The burning rate of the binder/AP/Al (40/45/15) composition was 0.991 cm/sec (0.39 in/sec) at 70.31 Kg/cm^2 (1000 psi) with a pressure exponent of 0.48 over the pressure range of 35.16 to 105.5 Kg/cm^2 (500 to 1500 psi). The density of the cured

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propellant was 1.81 gm/cc (0.0654 lbs/in³) for 60% solids loading (AP/Al, 45/15) and 1.865 gm/cc (0.067 lbs/in³) for 65% solids (49/16). Impact sensitivity tests indicated that the propellant was less sensitive than double-base propellants and the vacuum stability at 120°C was 0.9 cc gas/gm/48 hrs.

Frozen and shifting specific impulses, I_{sf} and I_{ss} respectively, and volumetric impulse I_v , were computed for a number of compositions based on the nitropolyester binder. The calculations were performed on the IBM 704 and 7090 computers, using an isenthalpic combustion and isentropic expansion from 70.31 to 1.03 Kg/cm² (1000 to 14.7 psi) assuming thermal and kinetic equilibrium between the gas and condensate particles.

A propellant composition containing binder/AP/Al (52/28/20) had a calculated I_{ss} of 268 seconds and a volumetric impulse of about 485 gm force sec/cm³.

Since this report was written a considerable improvement in the physical properties of the binder has been made. The substitution of other crosslinking agents for the epoxides and the use of improved nitropolyesters has increased the tensile strength and elongation of the binder by about 5% and 300%, respectively, over the maximum values given in this report. These improved compositions will be presented in a later report.

SECTION A. PREPOLYMER DEVELOPMENT

I. INTRODUCTION

A. Criteria of Desirability for High Energy Binders

In the synthesis of any new high energy binder system for explosive or propellant applications, a number of a priori requirements must be taken into account. The practical test in the present instance is the ability of the BEANSTALK* system to satisfy these requirements.

1. The binder** system should contain as much energy as possible. By incorporating the maximal number of oxidizing groups in the binder, the amount of inorganic oxidizer which need be added to achieve optimal specific impulse is decreased with consequent lowering of total solids loading. This may result in improved physical properties at any level of ballistic performance.

2. The solubility of plasticizer in both prepolymer*** and binder should be as great as possible. The relatively low molecular weight plasticizer is intrinsically capable of carrying more high energy groupings than the other binder components. Thus, the greater the amount of plasticizer which may be incorporated without exudation from or degradation in physical properties of the end-product, the more readily satisfied is criterion I.A.1.

3. Complete cure should be attainable under the mildest possible conditions for reasons of safety and for convenience of operation (e.g., to minimize shrinkage). The cure reaction should not be overly exothermic. No co-product or by-product such as water, carbon dioxide or nitrous fumes should be formed during the cure reaction. The latter condition is to preclude gassing which has serious effects on physical properties.

* Code name for the NOL propellant binder or a propellant containing this binder.

** Binder = Prepolymer solution plus curing agent and catalyst, Prepolymer solution = nitropolymer + FEFO

*** Prepolymer = Nitropolyester

4. The system should incorporate a number of parameters whose variation would be expected to influence the physical properties of the end-product in a predictable direction. Such parameters might include: molecular weight and functionality of the prepolymer; amount of plasticizer; amount, molecular weight and functionality of the curing agent. End-product properties should be relatively independent of parameters which may be difficult to reproduce closely on scaling up such as the conditions of the prepolymer-forming reaction and the conditions of cure. End-product properties should be relatively insensitive to the effects of adventitious impurities.

5. Mutual compatibility of all components of the binder system is a sine qua non. Otherwise physical and ballistic properties may change in storage. The binder system should also be compatible with as wide a variety of oxidizer types and fuel types as possible.

6. The overall system and all components should be insensitive and thermally stable.

7. All ingredients should be cheap or potentially cheap.

B. Information and Guidelines on Nitroaliphatic Polymers

Work at NOL and elsewhere during the past several years has furnished a large body of information on high energy polymer systems¹. From this and from a general knowledge of polynitroaliphatic chemistry the following facts were considered pertinent and served as guidelines in the syntheses leading to the BEANSTALK system.

1. Strongly basic or nucleophilic reagents cause degradation of polynitroaliphatic systems. To satisfy requirement I.A.5 the prepolymer-forming and cure reactions must be acid catalyzed or uncatalyzed. Amine groups must be avoided.

2. At comparable oxidant balances or comparable levels of performance, pure compounds containing the $C(NO_2)_3$ - linkage are more sensitive and less thermally stable than compounds containing the $-C(NO_2)_2$ - or $FC(NO_2)_2$ - linkages². Compounds of the latter types are also generally less reactive at the nitro functions. Similar effects would be expected to apply in polymeric systems.

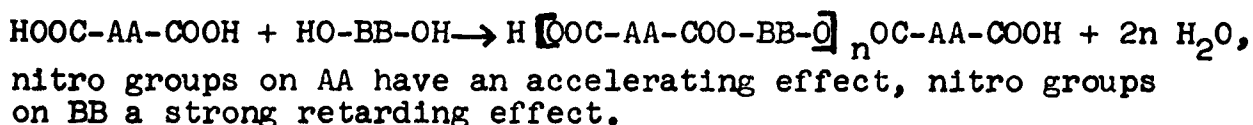
3. The $-N(NO_2)-$ grouping is believed to be a "trigger" linkage as concerns both sensitivity and thermal stability of pure compounds³ and it might also be profitable to avoid this linkage in polymer systems.

4. ~~C~~-Nitro groups inhibit radical polymerizations.

5. Polyethers have generally shown poor compatibility with trinitromethyl compounds and only marginal compatibility with gem-dinitromethyl and fluorodinitromethyl compounds. This is due to peroxides formed by air oxidation of the ether linkage.

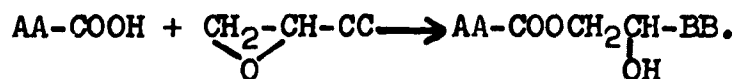
6. Polyesters appear to show excellent compatibility with nitroaliphatic compounds.

7. In the acid-catalyzed reaction,



8. Preparation of polyester polymers by reaction I.B.7 alone is complicated by the fact that the co-product water becomes increasingly difficult to remove as reaction progresses and the product becomes more viscous. This factor would conflict with requirement I.A.3. Prepolymers may be formed by the above reaction providing the prepolymer molecular weight is not too large and care is taken to remove all water of reaction prior to the cure.

9. Nitro groups on AA also accelerate the acid catalyzed reaction.



No co-product is formed so that this might serve as a cure reaction without conflicting with requirement I.A.3.

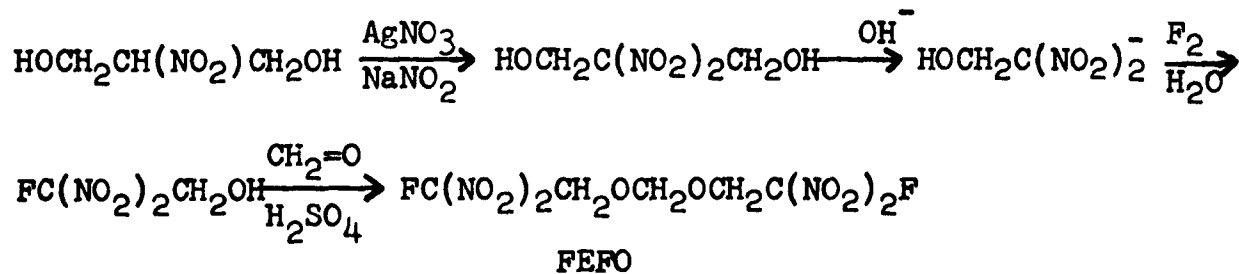
10. Esters of nitroalcohols are readily transesterified by non-nitro-containing alcohols. If reaction I.B.9 is used in the cure, free hydroxyl groups are generated in the end product. The presence of esters of nitroalcohols in the system might introduce problems relating to requirement I.A.5 (this is the reason why bis(2,2-dinitro-2-fluoroethyl) carbonate was not used in combination with FEFO as a plasticizer).

C. BEANSTALK Ingredients. Preparation and Potential Availability

1. The Plasticizer, FEFO. One of the more promising high energy plasticizers now available is FEFO, bis(2,2-dinitro-2-fluoroethyl) formal. FEFO is a result of the combined efforts of Aerojet-General and NOL. NOL was the first to predict that fluorodinitromethyl compounds would show improved sensitivity and thermal stability properties relative to other polynitro-aliphatic compounds. Members of this class were first synthesized at NOL by the reaction of salts of the corresponding 1,1-dinitro compounds with perchloryl fluoride⁴. One such compound first synthesized at NOL was 2,2-dinitro-2-fluoro-ethanol but, after a number of trials, the maximal yields obtained by the perchloryl fluoride route were no higher than 25% and purification was difficult. It was thought at NOL that the perchloryl fluoride route would never provide a commercially feasible method for the preparation of this material.

Also discovered at NOL was the method of reacting polynitroalcohols with formaldehyde in sulfuric acid to form the formals. Representative formals first synthesized in this manner at NOL were bis(2,2,2-trinitroethyl) formal, TEFO, and bis(2,2-dinitropropyl) formal⁵.

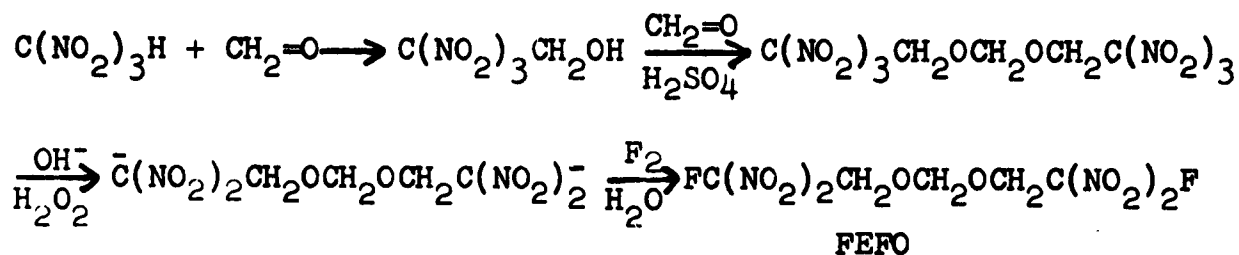
With the discovery by Grakauskas at Aerojet of the aqueous fluorination method, a high-yield procedure for the preparation of dinitrofluoroethanol became available. FEFO was first prepared by Aerojet by applying the NOL formal procedure to this alcohol. The method developed at Aerojet and carried through the pilot-plant stage involved the following sequence of steps.



The overall yield was quite good. The only disadvantage was that the cost of FEFO was governed by that of 2,2-dinitropropanediol-1,3. This compound, prepared by the oxidative nitration method is intrinsically expensive and it would be

difficult to project a cost lower than \$5 per lb. for FEFO prepared by this route.

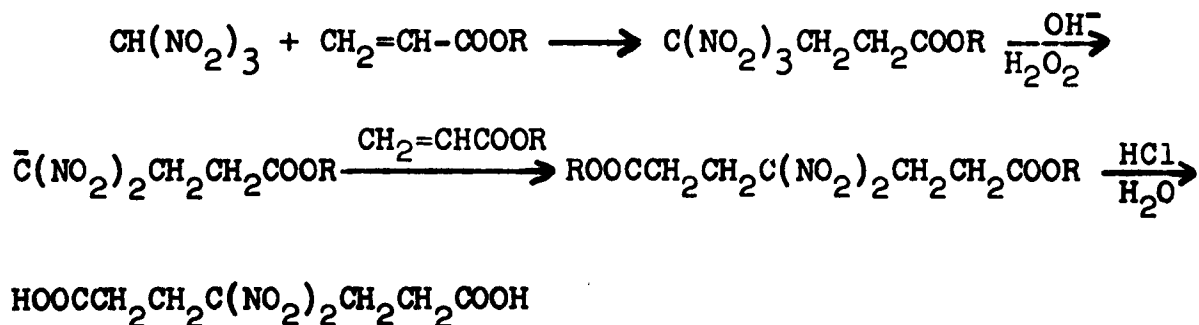
NOL returned to the picture with the development of an alternative route which takes advantage of the Grakauskas aqueous fluorination method, but which depends on the potentially cheap nitroform as the starting material. This route involves the alkaline hydroperoxide reduction of TEFO to the dipotassium or disodium salt of bis(2,2-dinitroethyl) formal⁶ and the aqueous fluorination of the latter compound⁷.



The overall yield (nitroform to FEFO) is about 50% and may be further improved by further process development. Based on 15-25 cent per lb. nitroform (a reasonable cost in large scale production⁸, \$1-2 per lb. would be an anticipated cost in bulk production of FEFO.

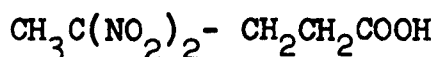
2. Prepolymer Components. a. 4,4-Dinitropimelic Acid

This compound, first invented in Germany during World War II⁹ is being made by a "one-pot" procedure developed at NOL¹⁰.



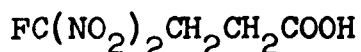
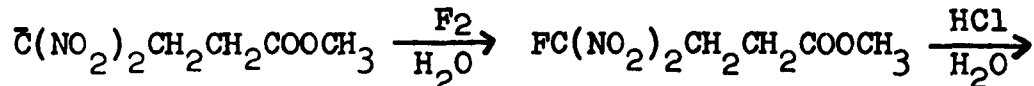
The anticipated cost of this material in large-scale production is \$1-3 per lb.

2.b. 4,4-Dinitrovaleric Acid. This product may be prepared by the reaction of 1,1-dinitroethane with methyl acrylate and subsequent hydrolysis. The overall yield is 60-70%.



1,1-Dinitroethane may be prepared by the ter Meer reaction of 1-chloro-1-nitroethane with sodium nitrite or by oxidative nitration of nitroethane. The former method is being pilot-planted at Hercules Powder Co., the latter method at Naval Propellant Plant. Potential cost is estimated at \$3-5 per lb.

2.c. 4,4-Dinitro-4-fluorobutyric Acid. This compound may be prepared by fluorination of a salt of methyl 4,4-dinitrobutyrate and subsequent hydrolysis. Aqueous fluorination and perchloryl fluoride have both proven efficacious in effecting the latter transformation¹¹.



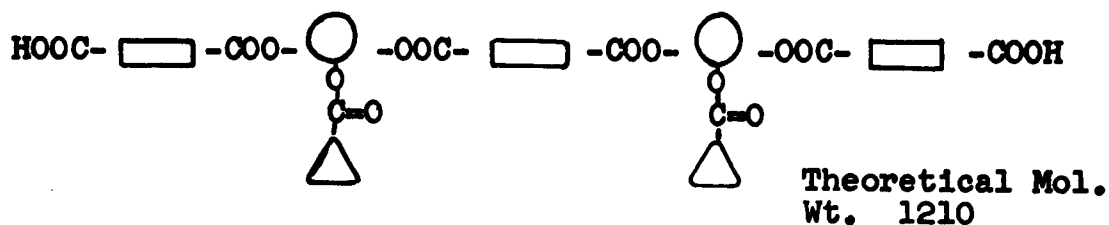
Estimated cost: slightly less than dinitropimelic acid.

II. DISCUSSION

A. Exploratory Research Leading to BEANSTALK. Prepolymer Structure

1. Pentamer. After a number of unsuccessful preliminary attempts to prepare a high energy polyester prepolymer from 4,4-dinitropimelic acid and 2,2-dinitro-1,3-propanediol (frustrated by the relative unreactivity of nitroalcohols in acid-catalyzed esterifications, see I.B.7), a material was found which could be cured to a rubbery product containing 50% plasticizer. This prepolymer was prepared by the

simultaneous p-toluenesulfonic acid catalyzed esterification of glycerol with both 4,4-dinitropimelic and 4,4-dinitrovaleric acids (Gly, DNPA, DNVA). The reaction went to 96-98% completion (as measured by water evolved) in four to six days if the reaction was carried out under (not in) a refluxing non-polar solvent at ca. 80°C and if the plasticizer was added to the reaction mixture when the esterification was 60-70% complete to lower the viscosity of the reacting phase (see I.B.8). Using a 3:3:2 ratio of DNPA:DNVA:Gly, this first product (labelled Pentamer) had the idealized dicarboxylic acid structure,



where,

$\text{HOOC}-\square-\text{COOH} = 4,4\text{-dinitropimelic acid}$

$\text{HOOC}-\triangle-\text{COOH} = 4,4\text{-dinitrovaleric acid}$

$\text{HO}-\bigcirc-\text{OH} = \text{glycerol}$
OH

It should be kept in mind that this and subsequent structures drawn for prepolymers are idealized or average representations and that the compositions represented are in reality extremely complex mixtures containing, in addition to small amounts of unreacted starting materials, varying amounts of miscellaneous condensation products of which the following are representative:

1 Gly-3DNPA (3), 1 Gly-2 DNPA (2), 1 Gly-1 DNPA (1),
1 Gly-3 DNVA (0), 1 Gly-2 DNVA-1 DNPA (1), 1 Gly-2 DNVA (0),
1 Gly-1 DNVA-2 DNPA (2), 2 Gly-5 DNPA (4) 2 Gly-4 DNPA (3),
2 Gly-4 DNPA-1 DNVA (3), 2 Gly-2 DNPA-3 DNVA (1), 2 Gly-1 DNPA-
4 DNVA (0), 3 Gly-4 DNPA (2), 3 Gly-5 DNPA-2 DNVA (3),

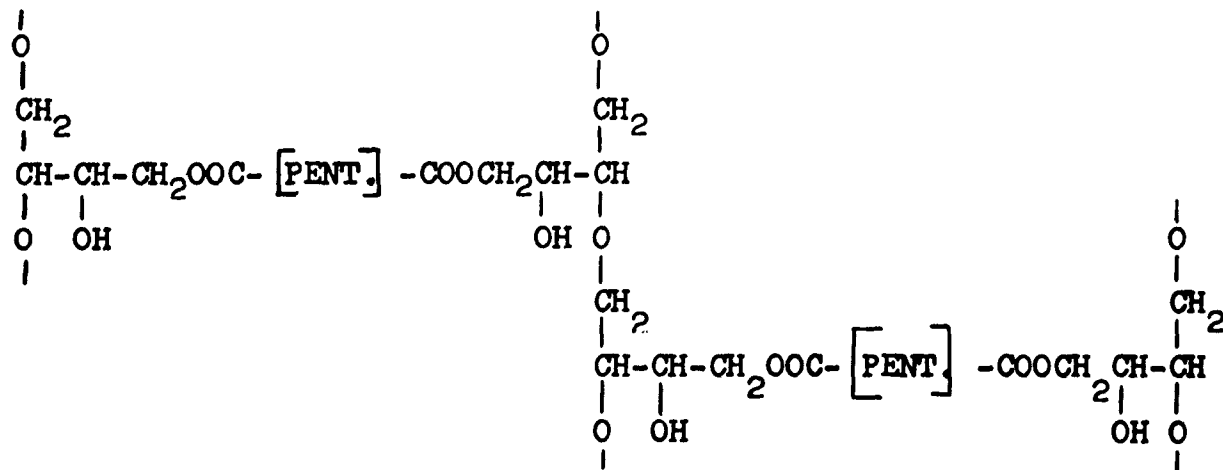
3 Gly-6 DNPA-1 DNVA (4), 3 Gly-7 DNPA (5), 4 Gly-5 DNPA-4 DNVA (2), etc. The number in parentheses represents the functionality (number of free carboxyl groups) in each species.

2. Curing of Pentamer. Preliminary Trials. Initial curing attempts involved a hydroxyl-terminated pentamer (from 2:3:3 DNPA:DNVA:Gly) and either 2,4-tolylene diisocyanate or 4,4'-diisocyanatodiphenylmethane with ferric acetyl-acetone as catalyst. The polyester-polyurethane products from these cures were viscous, semi-rubbery materials, quite sticky to the touch. There was extensive bubble formation in the mass, indicating that such a system might not fulfill requirement I.A.3.

Subsequent trials involved the Pentamer from II.A.1 with a polyepoxide curing agent, butadiene diepoxide (BDDO). It was expected that using a 2:1 molar ratio of BDDO to Pentamer the most rapid reaction would be that in I.B.9 and that the initial product might be represented by the idealized structure,



The subsequent reaction would be polyether formation from the above long-chain diepoxide to form



When the Pentamer from II.A.1 containing 50% FEFO and BDDO were allowed to react at 70-80°C a rubbery polymeric material was formed. The reaction, carried out in the absence

of cure catalyst, required seven to eighteen days and there was no evidence of bubble formation in the product. The physical properties of this material looked promising at the time, although they were poorer than products which were later prepared. There was no indication of FEFO exudation even at elevated temperatures and thermal stabilities were in the range of 2-3 cc of gas per gram per 48 hours at 120°C.

Exploratory trials were also made using vinylcyclohexene dioxide (VCDO) as curing agent, again in the absence of cure catalyst. After three days at 98°C a product of seemingly similar physical properties was obtained.

3. Termination of Exploratory Research Phase. The physical properties of these initial products seemed sufficiently promising and their mode of preparation sufficiently simple to suggest the termination of the exploratory research aspect of the program and the beginning of a process and product development phase. It was decided that the BEANSTALK binder system would be based on prepolymers prepared from glycerol, dinitropimelic and dinitrovaleric (later 4,4-dinitro-4-fluorobutyric) acids, would incorporate FEFO as plasticizer and would be cured with a diepoxide.

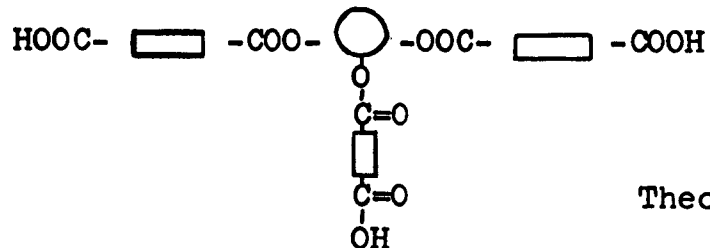
B. Development Work on BEANSTALK Prepolymers

1. S-Tricarboxylic Acid. If the alcohol + acid \rightarrow ester reaction (I.B.7), the acid + epoxide \rightarrow hydroxyester reaction (I.B.9) and the epoxide \rightarrow ether reaction (II.A.2) had all been quantitative or near quantitative, the products described in II.A.2 would be expected to be very highly crosslinked, thus hard and brittle. The fact that these products were instead rubbery suggested that these transformations, especially the polyether-forming reaction, were far from quantitative. It was also found that, while a typical batch of Pentamer cured nicely with BDDO in seven days at 70°C, occasional batches remained liquid after twice this time at similar temperatures. This indicated that, in addition to being less than quantitative, the polyether-forming crosslinking reaction was not readily reproducible and posed a potential conflict with requirement I.A.4.

For this reason an attempt was made to minimize ether formation and to take advantage of the more rapid (and presumably more reproducible) hydroxyester forming reaction (I.B.9) for both chain-extension and crosslinking. To this end a trifunctional (tricarboxylic acid) material was required which, in admixture with Pentamer, would provide the desired

amount of crosslinking. In addition to providing a more reliable crosslinking mechanism, the ratio of trifunctional to difunctional material would be an additional parameter whose variation would be expected to influence end-product properties (see requirement I.A.4).

The first such trifunctional material prepared was a condensation product of glycerol with 3 moles of dinitro-pimelic acid. Using the previous conventions, the idealized structure of this material (labelled S-Tricarboxylic Acid) is

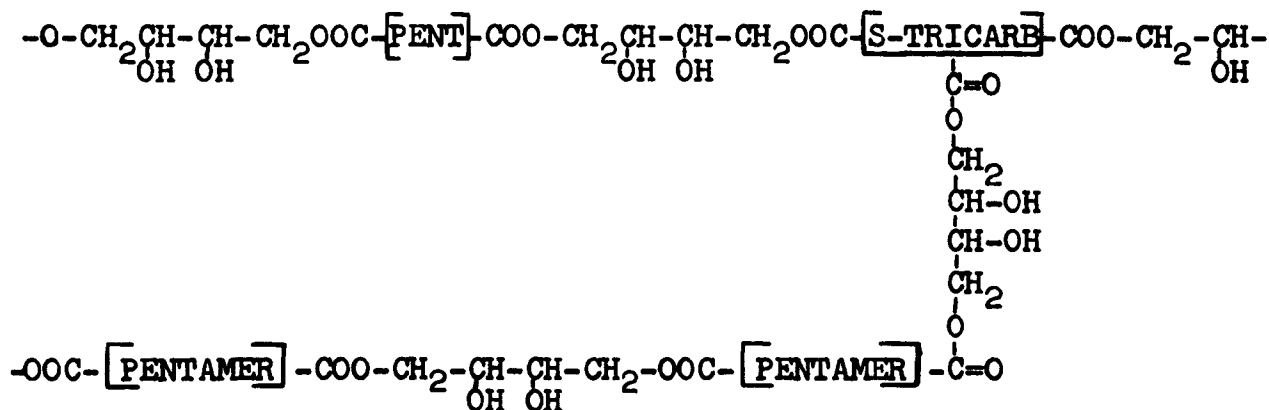


Theoretical Mol. Wt.
788

The preparative method for S-Tricarboxylic Acid was similar to that for Pentamer.

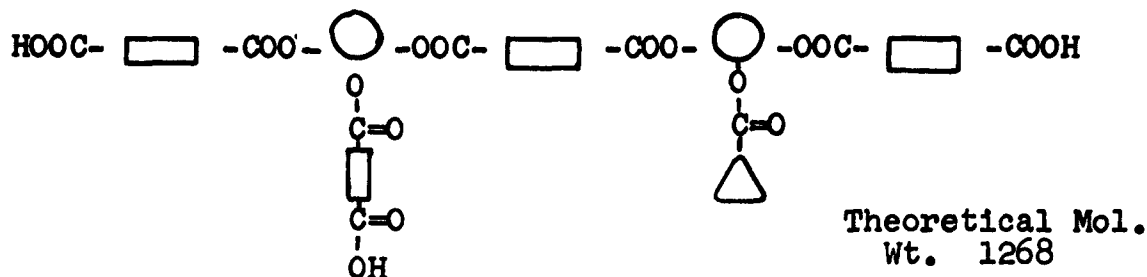
That this material did indeed provide a more reliable crosslinking mechanism was indicated by the fact that physical properties of diepoxide-cured S-Tricarboxylic Acid-Pentamer mixtures varied in a predictable manner with the tricarboxylic acid: dicarboxylic acid ratio.

A portion of an idealized structure for a Pentamer-S-Tricarboxylic Acid-BDDO polymer may be represented by:



2. T-Tricarboxylic Acid. As a consequence of difficulties encountered in scaling up the S-Tricarboxylic Acid preparation (see III.B.) an additional tricarboxylic acid was prepared for evaluation using 4:1:2 ratios of DNPA, DNVA and Gly. This

material (labelled T-Tricarboxylic Acid) has the idealized structure,



T-Tricarboxylic Acid proved to be more convenient to use than S-Tricarboxylic Acid (lower viscosity, more homogeneous mixtures with Pentamer) and provided end-products with physical properties at least as satisfactory (see section B of report). No difficulties were encountered in scaling up this preparation.

3. TF-Tricarboxylic Acid. An analog of T-Tricarboxylic Acid was prepared using 4,4-dinitro-4-fluorobutyric acid in place of 4,4-dinitrovaleric acid. Advantages of this material relative to the above are (a) slightly higher oxidant balance, (b) fluorodinitrobutyric acid is potentially cheaper than dinitrovaleric acid in bulk production. Physical properties of T-Tricarboxylic and TF-Tricarboxylic Acid-containing polymers and prepolymers were similar.

4. Attempts to Use CARFO. 4,4,10,10-Tetranitro-6,8-dioxatridecanedioic acid (CARFO), an interesting new dicarboxylic acid first prepared at NOL¹², seemed to offer a number of potential advantages relative to dinitropimelic acid, i.e., higher proportion of nitro groups, greater chain length of prepolymer. A batch of Pentamer analog was prepared using this material, but the product showed an abnormally low neutralization equivalent¹³, and was not readily curable. Further work with CARFO is anticipated in the future.

5. Attempt to Use 4,4,4-Trinitrobutyric Acid. A single attempt to use trinitrobutyric acid in place of dinitrovaleric acid to make a Pentamer analog resulted in extensive decomposition during the prepolymer preparation and further decomposition in the course of an attempted cure. The amount of water evolved was 85% of theoretical.

C. Miscellaneous Observations, Calculations, Conclusions

1. Preliminary Performance Calculations. We have carried out a number of pertinent calculations for the preliminary composition represented in II.A.2 with 50% FEFO as plasticizer.

$$\Delta H_f \text{ of FEFO} = 171 \text{ Kcal/mole} = -26.7 \text{ Kcal/50 g.}$$

assuming C-F bond = 100 Kcal. and $\Delta H_{\text{vap.}} = 20 \text{ Kcal/mole}$

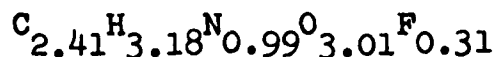
$$\Delta H_f \text{ of polymer} = -1035 \text{ Kcal/mer} = -37.5 \text{ Kcal/50 g.}$$

where 1 mer = 1 pentamer + 2 BDDO and assuming

$$\Delta H_{\text{subl.}} = 10 \text{ Kcal/100 g.}$$

$$\Delta H_f \text{ of BEANSTALK} = -64.2 \text{ Kcal/100 g.}$$

Elemental composition of BEANSTALK per 100 g. =



2. Energy Content Relative to Non-Nitro Binders. The question has arisen as to whether it is worthwhile attempting to incorporate nitro groups in the polymer backbone or whether the purpose might not be served as well by using larger proportions of high energy plasticizer with non-nitro containing polymers. The following comparison is illustrative.

Mol. Wt. of 1 Pentamer + 2 BDDO (Composition II.A.2)

= 1382; $-\text{CH}_2\text{C}(\text{NO}_2)_2-$ moiety is at about same oxidant balance as FEFO (1 H_2O , 1 CO , 1 CO_2)

1 Pentamer contains 5 $\text{CH}_2\text{C}(\text{NO}_2)_2$ moieties. Combined

Mol. Wt. of five such moieties = 590 g.

1382 g. BEANSTALK + 1382 g. FEFO (50:50) equivalent in oxidizing capacity to 1972 g. FEFO + 792 g. non-nitro polymer (72:28)

SECTION B. POLYMERIZATION STUDIES

I. INTRODUCTION

Polymerization studies have been carried out on the nitropolyesters described in Section A of this report. Qualitative observations were made on 5 gram batches mixed by hand in small glass bottles. The polymer was cast into small aluminum weighing dishes which had been coated with a Teflon film. The samples were then deaerated and placed in an oven to cure. Observations were made as the cure progressed. After the cure was completed, the sample was removed from the dish and the strength and elongation were evaluated by visual comparison with other samples.

Tensile test specimens were prepared in a gumstock mold consisting of two polished Teflon-coated stainless steel plates. The plates were separated by a 0.19 cm (0.075") thick Teflon gasket in which a space 7.62 x 12.7 cm (3" x 5") had been cut. The binder ingredients were mixed by hand in a beaker, deaerated, cast into the space in the gasket and further deaerated. The top was then placed on the mold and held in place with steel pegs. The entire mold was placed in a tray and put into the curing oven. A thermocouple, placed under the mold, was used to control the cure temperature.

The tensile specimens were cut from the gumstock sheet with an ASTM D412 die "C". This die is 11.33 cm (4.5") long and 2.54 cm (1") wide. The critical width of the "dogbone" is 0.635 cm (0.250") and the gage length is 2.54 cm (1"). The specimens were tested on an Instron testing machine at a loading rate of 50.8 cm (20") per minute. Elongation was measured both by the crosshead motion and a ruler held next to the specimen.

The formulations were made up on the basis of two characteristic ratios. The Carboxy/Epoxy ratio was the ratio of the number of equivalents of acid to the number of equivalents of epoxy. The Dicarb/Tricarb ratio was the ratio of the number of equivalents of the dicarboxylic component to the number of equivalents of the tricarboxylic component.

The amount of plasticizer was arbitrarily fixed at 50% and all mixes were formulated to contain this amount of FEPO. The percent plasticizer was held constant until the other cure parameters were evaluated.

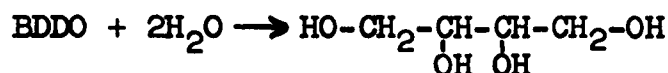
II. DISCUSSION OF RESULTS

A. Qualitative Evaluation

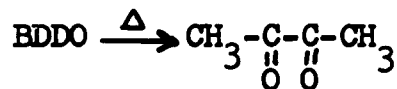
1. Epoxy Crosslinking Agents

Preliminary work indicated that the pentamer could be cured with butadiene dioxide to a rubbery polymer. The cure required 14 days at 70°C. The material, although flexible, was quite weak. By adding 2% stannous octoate as a catalyst the cure time was reduced to 48 hours at 60°C. A number of curing studies were made to evaluate BDDO as a crosslinking agent for the nitropolyesters. It was concluded that BDDO was unacceptable for this purpose because:

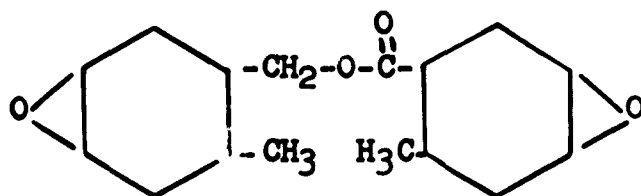
- (a) Reproducible cures could not be obtained.
- (b) BDDO is hydrolyzed by water to form erythritol.



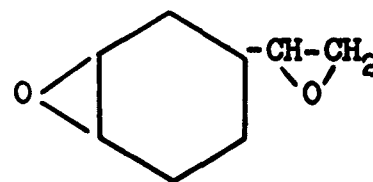
- (c) BDDO can isomerize when heated in the presence of acids to yield among other products, diacetyl.



A second compound, vinyl cyclohexene dioxide (VCDO) was not only more reactive than BDDO but was a more reliable crosslinking agent for the nitropolyesters. The use of a third epoxy crosslinking agent, Epoxide 201, produced an elastomeric binder with the best balance of physical properties. As shown below, Epoxide 201 has two epoxide groups of virtually equal reactivity.



Epoxide 201



Vinylcyclohexene
dioxide

It seems likely, therefore, that in the early stages of curing when the binder is still liquid, very long chains might be formed since both ends of the epoxy crossliner are readily reactive with carboxy groups. Since the cyclic epoxy group is inherently more reactive under acid conditions than the open chain epoxy group it would appear that more crosslinking would occur later in the cure reaction than is possible with VCDO.

With VCDO the main part of the reaction will occur initially at the cyclic epoxide group. The reaction in the early stages would most likely consist of esterification of the epoxy group with carboxy groups, followed by etherification of the resulting hydroxy groups with other epoxy groups. This reaction would lead to more crosslinking and less chain building in the all important early stages of polymerization.

The epoxide equivalents of the above curing agents were determined by titration with HBr in glacial acetic acid using crystal violet as the indicator¹⁴. The epoxide equivalents of the curing agents used in the gumstock formulations are shown in Table I.

2. Acid Catalysts

It was found that stannous octoate was unsuitable as a catalyst because it reacted with the FEFO. Therefore, a number of other acid catalysts were evaluated for their effectiveness in accelerating the cure of acid-terminated polyesters with epoxies.

- (a) ZnCl_2 was only slightly effective.
- (b) SnCl_4 was very active; so much so that it could not be used.
- (c) H_3PO_4 was active but was only slightly soluble in the prepolymer solution.
- (d) Boron trifluoride-ethyl ether complex ($\text{BF}_3 \cdot (\text{Et})_2\text{O}$) was an active catalyst which was soluble in and compatible with FEFO. This was the preferred catalyst and it was added to the binder ingredients as a 2% solution in FEFO.

3. Cure Studies

A number of curing studies were made using various combinations of prepolymer, diepoxide curing agents and catalyst. Through purely qualitative, visual observation of

these mixes the following tentative conclusions were reached:

- (a) The pentamer alone would not provide sufficient acid functionality to produce binders with good physical properties.
- (b) The functionality needed could be obtained by adding a trifunctional polyester, S-Tricarboxylic acid.
- (c) The pentamer with the functionality increased by the addition of S-Tricarboxylic acid and catalyzed with $\text{BF}_3 \cdot (\text{Et})_2\text{O}$ could be cured in 72 hours at 60°C .
- (d) The best balance of physical properties was obtained with a Carboxy/Epoxy ratio of 0.75 and a Dicarb/Tricarb ratio of 3.00.

When quantitative gumstock tests were performed the last observation (d) required some modification.

Further qualitative work was carried out concurrently with the quantitative gumstock tests.

A number of different small mixes were made up with the T-Tricarboxylic acid cured with VCDO. These compositions were similar to gumstock compositions which had been tested. The following visual observations were made:

- (a) The tensile strength increased and % elongation decreased when the FEFO content was lowered from 50 to 46.5%.
- (b) The strength dropped with a slight increase in elongation when the FEFO content was raised from 50 to 55.0%.
- (c) The strength increased slightly and elongation decreased with an increase in the relative amount of epoxy. With decreased epoxy the opposite effect was noted.
- (d) A catalyzed composition of T-Tricarboxylic acid and EP201 cured in 74 hours at 50°C .
- (e) An uncatalyzed composition of T-Tricarboxylic acid (same as (d)) cured in 120 hours at 60°C , and 250 hours at 50°C . The uncatalyzed material was somewhat weaker than the catalyzed material.

B. Gumstock Tests

The results of all of the tensile tests performed on the BEANSTALK binder are shown in Table 1. It should be noted that until these tests were performed we had very little idea of what the qualitative observations meant and even less of an idea what the finished propellant would be like.

A large mix was made for a gumstock sample (Mix 223-R) using the composition which by qualitative observation appeared to have the best balance of physical properties. It cured in 72 hours at 60°C to a good quality, rubbery sheet. The tensile strength of this sheet was poor but elongation appeared to be quite adequate.

Mix 231-R did not measure up to expectations. Both the elongation and the tensile strength dropped by a considerable amount as compared to Mix 223-R. Since the functionalities of both prepolymer ingredients in Mix 231-R were higher it would be expected that the elongation would drop but that the tensile strength would increase. It is possible that the lower strength was caused by a premature failure due to inhomogeneity of the test sample. Batch No. 2 of the S-Tricarboxylic acid contained only 33.5% FEFO and was therefore much stiffer and harder to mix than batch No. 1.

Propellants made with a binder composition like that of Mix 231-R were very soft and could not be machined into tensile test specimens. One propellant mix with a Carboxy/Epoxy ratio of 0.56 was made. This propellant was marginally machinable and a tensile specimen could be prepared.

Mix 242-R differed from 231-R in having both a lower prepolymer functionality and a lower carboxy/epoxy ratio. Predictably, the strength of 242-R was greater than that of 231-R.

Mix 244-R was made to evaluate the use of T-Tricarboxylic acid as a binder by itself. Since by using only the T-Tricarboxylic acid the functionality of the polymer was greatly increased, relatively less epoxy was needed to provide crosslinking. The results were very encouraging since the same strength was obtained as in Mix 242-R with much better elongation.

Mix 254-R was the same as Mix 244-R except that a different batch of T-Tricarboxylic acid was used. As expected from the lower functionality of the prepolymer, the strength was somewhat

lower than Mix 244-R while the elongation was higher.

Mix 255-R is identical with Mix 254-R except for the use of Epoxide 201 instead of the vinyl cyclohexene dioxide. The dramatic increase in tensile strength is accompanied by a moderate drop in elongation as compared to Mix 254-R.

Mix 256-R had both a lower tensile strength and elongation as compared to 255-R. The loss in strength was predictable since the overall acid functionality was lower. The lower elongation is probably not too significant but does indicate that there is no simple relationship between tensile strength and elongation in this highly plasticized system.

Table II lists some additional properties of the cured binder.

TABLE I
POLARIS PROPELLANT BINDER GUMSTOCK TESTS

| Mix Number | 223-R | 231-R | 231-R | 242-R | 244-R | 254-R | 255-R | 256-R |
|-------------|--|-------------|-------|-------|-------|-------|-------|-------------|
| Carboxy | 0.77 | 0.75 | 0.75 | 0.60 | 1.00 | 1.00 | 1.00 | 0.75 |
| Epoxy | | | | | | | | |
| Dicarb | 2.70 | 3.00 | 3.00 | 3.00 | 0 | 0 | 0 | 3.00 |
| Tricarb | | | | | | | | |
| INGREDIENTS | Wgt.% | 73.8 | 76.9 | 76.9 | 67.33 | 0 | 0 | 60.19 |
| | Batch # | 1 | 2 | 2 | 4 | - | - | 4 |
| | Func. | 1.68 | 1.85 | 1.85 | 1.69 | - | - | 1.69 |
| | Wgt.% | 13.1 | 8.1 | 8.1 | 16.44 | 84.08 | 83.60 | 72.18 |
| | Type | S | S | S | T | T | T | T |
| | Batch # | 1 | 2 | 2 | 2 | 2 | 3 | 2 |
| | Func. | 2.51 | 2.74 | 2.74 | 2.60 | 2.60 | 2.45 | 2.60 |
| | Wgt.% | 9.3 | 8.6 | 8.6 | 10.34 | 7.96 | 8.20 | 13.91 |
| | Type | VCDO | VCDO | VCDO | VCDO | VCDO | VCDO | Epoxide 201 |
| | Epox. Eq. | 74 | 74 | 74 | 74 | 74 | 74 | 145 |
| | | | | | | | | 145 |
| | Elongation at Break (E_b) (Cross Head) | 357% | 223% | 288% | 134% | 211% | 296% | 214% |
| | Elongation at Break (M_{e_b}) (Measured) | 170% (est.) | 103% | 129 | 65% | 100% | 142% | 104% |
| | $\frac{E_b}{M_{e_b}}$ | 2.1 (est.) | 2.2 | 2.2 | 2.1 | 2.1 | 2.1 | 2.4 |
| | Tensile Strength (psi) (S_b) | 14 | 6.7 | 9.4 | 26.8 | 26.8 | 21.5 | 67.2 |
| | Modulus S_b/M_{e_b} (psi) | 8.2 | 6.5 | 7.3 | 41 | 27 | 15 | 65 |
| | | | | | | | | 45.5 |

POLARIS PROPELLANT BINDER

Gumstock Tests

Explanation of Table I.

- (1) Sufficient FEFO was added to each formulation so that the composition contained 50.0% FEFO.
- (2) The catalyst used was a 2% solution of $\text{BF}_3 \cdot (\text{Et})_2\text{O}$ in FEFO. All compositions contained 1.5% of the catalyst solution or 0.03% $\text{BF}_3 \cdot (\text{Et})_2\text{O}$.
- (3) All compositions were cured for 72 hours at 60°C except for 255-R which was cured for 86 hours.
- (4) All test specimens were cut from a sheet 0.1905 ± 0.13 cm thick with an ASTM D412 die "C". The gage length of this die is 2.54 cm and the width is 0.635 cm.
- (5) Three specimens were tested of each composition except for 223-R of which two were tested.
- (6) The testing speed was 50.8 cm/min (20"/min) except for 231-R which was tested at 5.08 cm/min (2"/min). The values obtained for 231-R were corrected by running test specimens of a SUBROC polyurethane gumstock at both speeds and multiplying the results of 231-R by the ratios found between 5.08 cm/min and 50.8 cm/min for the polyurethane binder.
- (7) The elongation (E_b) was measured from the chart of crosshead motion vs. tensile stress. The actual elongation of the 2.54 cm gage length (Me_b) was measured with a ruler held to the specimen as it was pulled.
- (8) The specimens were tested on an Instron testing machine at a temperature of 25.6°C and a relative humidity of 50%.

TABLE II

PROPERTIES OF CURED PROPELLANT BINDER

| Mix No. | Impact Sensitivity (35 mg cubes) | | Vacuum Stability (cc gas/gm/48 hrs) at 120°C | Density (gm/cc) |
|------------|-------------------------------------|------|--|----------------------|
| | cm | S* | | |
| 231-R | 314 | 0.07 | 2.6 | -- |
| 223-R | >320 | -- | -- | $D_4^{27.6} = 1.500$ |
| TNT | 150 | -- | -- | -- |

*Standard deviation in log units.

SECTION C. PROPELLANT PROCESSING, PHYSICAL AND
BALLISTIC CHARACTERISTICS

I. TECHNICAL DISCUSSION

A. Processing BEANSTALK Propellant

(1) General Information

Composite propellant formulations containing new, high energy, nitropolyester binder systems have been processed and their physical properties determined. These propellants contained AP oxidizer, Al fuel, BEANSTALK prepolymer, FEFO plasticizer, VCDO chain extender and cross-linker and $\text{BF}_3 \cdot (\text{Et})_2\text{O}$ catalyst.

The AP was American Potash Chemical Co. propellant grade and was used either "as received" with an average particle size of 150 to 200 microns or after being ground in a Mikropulverizer to an average particle size of 25 microns. The aluminum used was either Reynolds 400 with an average particle size of 10 microns or Reynolds 1-511 with an average particle size of 26 microns.

Processing information was obtained on formulations containing 70, 65 and 60 weight percent solids loading (AP/Al), although later calculations indicated that the composition at maximum Isp was binder/AP/Al (52/28/20). The order of ingredient addition to the mixer and the mixing conditions were selected on the basis of information which was obtained from processing small laboratory size batches of propellant, taking into consideration the chemical reactions expected and using common composite propellant processing techniques. The size of the batches ranged from 50 to 600 grams. These batches were mixed in small sigma mixers, under vacuum and at controlled temperatures. To date 4050 grams of BEANSTALK propellant have been formulated and processed.

(2) Batch Processing

Prior to propellant formulation, some of the ingredients (AP, Al, VCDO and BF_3 catalyst solution) were weighed into separate containers. The prepolymer solution and FEFO were premixed and weighed together before addition to the sigma mixer.

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The aluminum, binder ingredients, and AP were added in that order and mixed under vacuum for ten to fifteen minutes. The mixer was then stopped, scraped down and the VCDO added. Mixing was continued for another ten to fifteen minutes, under vacuum. The mixer was stopped again, scraped down and the catalyst added. Mixing was continued for an additional fifteen to twenty minutes, under vacuum. Water at 50°C was circulated through the mixer jacket during the mixing cycle. It may be desirable to premix the Al and binder ingredients for larger batches but this was not done in formulating the small laboratory mixes. All the mixing was done remotely.

After mixing, the propellant was transferred from the sigma mixer to a casting can, deaerated through a slit plate and vacuum cast or bottom loaded into a mold under atmospheric pressure. If the propellant did not move easily through the slit plate, nitrogen gas pressure (up to 2.8 Kg/cm² or 40 psig) was used to help force it through. Nitrogen gas pressure (up to 3.5 Kg/cm²) was also used to force propellant into molds during bottom filling operations. The amount of pressure necessary depended on the amount of flow restriction and on the propellant viscosity. During deaeration of pound size mixes through 0.079 cm plates, atmospheric pressure was usually sufficient. Nitrogen pressure of 1.4-2.8 Kg/cm² was used to bottom load propellants into soda straws. However, bottom loading under vacuum into rectangular molds (for tensile specimens) with a cross section of about 2.54 cm by 3.175 cm required less than atmospheric pressure to load the propellant. When processing the uncured BEANSTALK propellant (deaeration and casting operations) a temperature of 50°C was maintained to keep the viscosity low. Higher temperatures may cause premature gelation of the propellant. The propellant was cured at 60°C for 72 hours.

The small scale processing indicates that typical BEANSTALK formulations containing up to 70 percent solids (AP and Al) can be processed and handled with conventional propellant equipment and techniques. No pot-life or viscosity measurements have been made but from observation both appear to be reasonable and adequate at the suggested processing temperature of 50°C. It is a matter of days before the propellants gelled when left uncured at room temperature.

(3) Toxicity

One point that should be brought out in connection with the processing of BEANSTALK propellants is that FEFO, the plasticizer, is toxic. When placed in the eyes of test animals, FEFO caused damage to the eye tissue¹⁸. It was also found that FEFO was adsorbed through the skin causing a sluggish effect in test animals. This effect wore off with time but there is no knowledge of the cumulative effects. Since the vapor pressure of FEFO is low at ambient temperatures, the use of rubber gloves, goggles and a hood or well-ventilated room should be adequate protection. FEFO has been used extensively by NOL personnel for over two years with no evidence of any toxic effects.

II. COMPOSITION OF THE BEANSTALK FORMULATIONS

Table III summarizes the composition of the BEANSTALK propellant formulations that have been processed. The pentamer, S-Tricarboxylic and T-Tricarboxylic acids contained a certain amount of FEFO which was added during synthesis. More FEFO was added with the catalyst which is a solution containing 98 percent FEFO and two percent $\text{BF}_3 \cdot (\text{Et})_2\text{O}$. Still more FEFO was added to the binder formulations to bring the plasticizer percentage up to 50 percent of the binder by weight.

Different batches of pentamer, S-Tricarboxylic and T-Tricarboxylic acids were used and these had different neutralization equivalents which required adjustment of the ingredient percentages to maintain the desired ratios. Propellant formulations Bean I-1,2 and Bean II-1 through 4 were formulated from pentamer batch #2 and S-Tricarboxylic acid batch #2. The formulations Bean II-5 and Bean III-1 were formulated from a mixture of pentamer batches #2 and #3 and from S-Tricarboxylic acid batch #2. Bean II-6, III-2 and IV-1 were formulated from pentamer batch #4 and T-Tricarboxylic acid batch #2. Bean V-1 and 2 were formulated from T-Tricarboxylic acid batch #3. Variations in solids loading of AP and Aluminum and the ratio and particle size distribution of these two ingredients were selected so that their effect on burning characteristics, processability and physical properties could be determined.

III. MECHANICAL PROPERTIES

Too few tests have been made thus far to be able to determine any definite correlations between the mechanical properties of the gumstock and the propellant but this correlation would be a useful tool. It might be expected that an improvement in the binder elongation or tensile strength will cause a similar improvement in the propellant containing that binder. It is not as easy to anticipate the quantitative relationship for instance, if 100 percent increase in binder elongation will produce 10, 15 or 20 percent improvement in propellant elongation. The results of testing the mechanical properties of several early batches of propellant are presented in Table IV.

It was not possible to obtain tensile specimens from several batches of the first formulations since their mechanical strengths were low. Initially it was hoped that the specimens could be machined but some compositions were too soft and attempts to prepare tensile specimens were unsuccessful. Die cut specimens could have been made, and in fact were made in one case. The results that were obtained substantiated the existence of rather low tensile strength in the first batches of propellant, particularly those batches with a 0.75 carboxy/epoxy ratio. Lowering this ratio improved the strength somewhat.

The mechanical testing of dogbone specimens was done with an Instron tensile testing machine. The crosshead speed was 5.08 cm per minute and the chart speed was 25.4 cm per minute. Testing was done at 21°C and at 50 percent relative humidity. It was intended that the specimens be dimensioned in accordance with the JANAF tensile test specimen specifications¹⁵ but because of the difficulty encountered in the machining operation the specimens that were used had a critical area or necked down portion that was 1.27 by 1.27 cm in cross section and which was 5.08 cm long, except for Bean II-4.

Only one tensile specimen was obtained for the Bean II-4 batch, therefore the mechanical properties indicated cannot be taken as representative of the system. However, they should indicate the order of magnitude of tensile strength and elongation. From these results it appeared that the tensile strength of the composition was only fair and that the elongation was rather low. Bean II-6, which had a higher carboxy/epoxy ratio (0.75 vs 0.56) exhibited good elongation but poor tensile strength. Bean IV-1 with a carboxy/epoxy ratio of 0.60 and using the T-Tricarboxylic acid in contrast

to Bean II-4 which used the S-Tricarboxylic acid had fair elongation and fair strength. Bean V-2 which consisted of T-Tricarboxylic for the acid component and which had a carboxy/epoxy ratio of 1.0 showed an improvement in elongation but a slight decrease in tensile strength over Bean IV-1.

These results indicated that while it was possible to get fair to good elongation with BEANSTALK propellant systems the tensile strengths were too low. Recent gumstock studies (Section B) have produced a binder system with greater strength than those reported in Table IV, an elongation greater than the binder used in Bean IV-1 and almost equal to the binder in Bean V-2. These improved mechanical properties resulted when Epoxide 201 was substituted for VCDO. The improved properties indicate that a propellant made from this binder at optimum binder content of 52% should have a maximum tensile strength of about 4.9 Kg/cm² (70 psi) at an elongation of over 25 percent. The elongation at maximum stress, referred to above, is an expected, actual elongation and not an elongation interpolated from the Instron crosshead travel alone.

The Shore A hardness values are approximate. These values were determined by hand holding the durometer, applying it rapidly to a flat propellant surface and holding it in place for ten seconds. The highest value indicated was recorded as an immediate hardness and the value indicated after 10 seconds was reported as the "10 second" hardness. No attempt was made to correlate the hardness values to other mechanical properties or to completeness of cure. It may be possible to determine later whether hardness can be correlated with some of the other properties of the propellant.

IV. PHYSICAL AND BALLISTIC PROPERTIES

Burning rate, density, hardness, impact sensitivity and vacuum stability were measured for different batches of propellant and are presented in Table V. Burning rate curves were obtained for three compositions over the pressure range of 35.16 to 105.5 Kg/cm² (500 to 1500 psi) and the pressure exponents calculated. These curves are shown in Figure 1.

The burning rate was generally measured on the uncured propellant and is the value reported unless stated otherwise. The uncured propellant was forced into 0.635 cm inside diameter soda straws which were X-rayed prior to being burned. Burning time was recorded for three adjacent, 5.08 cm intervals. The rate over each of these three intervals was calculated,

averaged and reported as a single value. Burning was carried out under nitrogen gas in a closed bomb at constant pressure.

The burning rates reported in Table V are average values for one to four straws burned at 70.31 Kg/cm² (1000 psi) pressure. The burning rate curves in Figure I represent data from a minimum of two and a maximum of four straws burned at each of the pressures (35.16, 52.7, 70.31 and 105.5 Kg/cm²) for each batch of propellant. The individual rates at one pressure were averaged and plotted as a single point.

Table V shows that Bean I-1 had a burning rate of 1.854 cm/sec (0.73 in/sec) at 70.31 Kg/cm². In this composition the AP was a 50/50 mixture of fine (25 microns) and "as received" (150 to 200 microns) while the Al averaged 10 microns. By changing the oxidizer blend to 30 percent "fine" and 70 percent "as received" and using Reynolds 1-511 aluminum (25 microns) the burning rate was decreased to 1.42 cm/sec (0.56 in/sec) for Bean I-2.

By using "as received" AP and 40 percent binder a burning rate of 0.988 cm/sec (0.389 in/sec) was achieved in batches Bean II-1, 2, 3 and 5, with a batch to batch variation of less than one percent. Bean II-4 was tested after it had cured in the straws. It had a burning rate of 0.9144 cm/sec (0.360 in/sec). This is slightly lower than the other uncured Bean II compositions with essentially the same solids loading and particle sizes. Propellants may unbond from the straw during cure exposing uninhibited areas. This can cause high apparent burning rates. The burning rates of the individual straws loaded with cured Bean II-4 were very consistent at each test pressure.

Bean III-1 contained 65 percent solids and had a slightly higher rate, 1.059 cm/sec (0.417 in/sec), than the compositions with 60 percent solids.

The burning rate curves for Bean II-5, Bean III-1, and Bean II-4 are shown in Figure I. Bean III-1 had a 65 percent solids loading and a slightly higher burning rate at all pressures than Bean II-5 which had a solids loading of 60 percent. Bean II-4 which had a solids loading of 61 percent had a lower rate than Bean II-5 because it was tested in the cured state. All the curves are essentially parallel and have a calculated slope, or pressure exponent of 0.48. The curves all appear to be straight lines, plotted on log graph paper.

Both the burning rate and the exponent were a little higher than desired and attempts will be made to lower these values by using small percentages of additives.

The density of these compositions was high because of the high density of the binder ingredients. Compositions with 60 percent solids loading (45/15, AP/Al) had a density of 1.81 grams/cc, while compositions with 65 percent solids (49/16, AP/Al) had a density of 1.865 grams/cc. These values are approximate since determinations were made on relatively small samples. Batch to batch variation in density was small. The density was determined from the physical dimensions of a piece of propellant and its weight in air.

An impact sensitivity test was made on two propellant compositions. The apparatus used was an ERL (Bruceton) impact machine with type 12 tools and a 2.5 kilogram drop weight. The values reported in Table V are the heights at which there is a 50% probability of an explosion. Details of the test method are covered in reference (16). Values have been reported for 35 milligram cubes of the propellant tested on bare tools. The results indicate that the BEANSTALK propellants are less sensitive to impact than one would anticipate for a high energy organic binder matrix with AP and aluminum. A Nitrasol formulation, H3515 (NC/Petrin/AP/Al, 15/35/35/15) had an impact sensitivity on bare tools of 20-25 centimeters.

The vacuum stability test is a measurement of the amount of gas evolved from a sample under vacuum at an elevated temperature, in this case 120°C. The test used is similar to the one described in reference (17). The results are reported in Table V as the number of cubic centimeters of gas evolved per gram for a specified length of time. The BEANSTALK propellant was tested for one week (168 hours) at 120°C and exhibited very good temperature stability evolving only 1.9 cc of gas per gram.

TABLE III
COMPOSITION OF FORMULATIONS

| Batch No. | AP fine | AP As Rec. | Al ¹ | Al ² | Pent. 3 | S-Tri. 4 | T-Tri. 5 | FEFO | VCDO | Cat. 6 | % Binder | Carboxy/Epoxy Ratio 7 |
|------------|---------|------------|-----------------|-----------------|---------|----------|----------|-------|-------|--------|----------|-----------------------|
| Bean I-1 | 27.5 | 27.5 | 15.0 | | 23.13 | 2.43 | | 1.41 | 2.58 | 0.45 | 30 | 0.75 |
| Bean I-2 | 16.5 | 38.5 | | 15.0 | 23.13 | 2.43 | | 1.41 | 2.58 | 0.45 | 30 | 0.75 |
| Bean II-1 | | 45.0 | | 15.0 | 30.84 | 3.24 | | 1.88 | 3.44 | 0.60 | 40 | 0.75 |
| Bean II-2 | | 45.0 | | 15.0 | 30.84 | 3.24 | | 1.88 | 3.44 | 0.60 | 40 | 0.75 |
| Bean II-3 | | 45.0 | | 15.0 | 30.84 | 3.24 | | 1.88 | 3.44 | 0.60 | 40 | 0.75 |
| Bean II-4 | | 45.7 | | 15.2 | 29.1 | 3.05 | | 2.01 | 4.32 | 0.62 | 39 | 0.58 |
| Bean II-5 | | 45.0 | | 15.0 | 30.52 | 3.35 | | 2.12 | 3.41 | 0.60 | 40 | 0.75 |
| Bean II-6 | | 45.0 | | 15.0 | 28.08 | | 6.86 | 1.00 | 3.46 | 0.60 | 40 | 0.75 |
| Bean III-1 | | 49.0 | | 16.0 | 26.69 | 2.95 | | 1.856 | 2.982 | 0.526 | 35 | 0.75 |
| Bean III-2 | | 49.0 | | 16.0 | 24.57 | | 6.0 | 0.88 | 3.025 | 0.525 | 35 | 0.75 |
| Bean IV-1 | | 45.0 | | 15.0 | 26.92 | | 6.58 | 1.76 | 4.14 | 0.60 | 40 | 0.60 |
| Bean V-1 | | 45.0 | | 15.0 | | | 33.44 | 2.68 | 3.28 | 0.60 | 40 | 1.00 |
| Bean V-2 | | 45.0 | | 15.0 | | | 33.44 | 2.68 | 3.28 | 0.60 | 40 | 1.00 |

Each batch contains 50% by wt. FEFO based on the binder except Bean II-4 which contains 49%. All formulations contained a dicarb/tricarb ratio of 3.00, except Bean V-1 and Bean V-2 which had a ratio of 0.

- 1 Aluminum used was Reynolds 400, average particle size is 10 microns.
- 2 Aluminum used was Reynolds 1-511, average particle size is 26 microns.
- 3 Pentamer (dicarboxylic acid) contains 53.3% FEFO.
- 4 S-Tricarboxylic acid contains 33.5% FEFO.
- 5 T-Tricarboxylic acid contains 50% FEFO.
- 6 Catalyst is boron trifluoride etherate (0.03% based on the binder) in a FEFO solution containing 98% FEFO and 2% $\text{BF}_3 \cdot (\text{Et})_2\text{O}$.
- 7 Ratios based on neutralization equivalents of the dicarboxylic and tricarboxylic acids determined by titration with base and on a measured epoxy equivalent for the VCDO of 74.
- 8 Fine AP has been ground to an average particle size of 25 microns; the "as received" AP has an average particle size of 150 to 200 microns.

TABLE IV
PROPELLANT MECHANICAL PROPERTIES

| Batch No. | % Binder | Carb/epoxy ratio | e_b % | e_m % | M_{eb} % | C_{em} % | e_b/M_{eb} | S_m psi | S_b psi | Mod psi | Remarks |
|------------|----------|------------------|---------|---------|------------|------------|--------------|-----------|-----------|---------|-----------------------------|
| Bean II-4 | 39 | 0.56 | 23 | 23 | | | | 42 | 42 | 244* | One test specimen machined. |
| Bean II-5 | 40 | 0.75 | | | | | | | | | Could not make specimens. |
| Bean II-6 | 40 | 0.75 | 64 | 52 | 46 | 39 | 1.35 | 26 | 23 | 67 | Three specimens die cut. |
| Bean III-1 | 35 | 0.75 | | | | | | | | | Could not make specimens. |
| Bean III-2 | 35 | 0.75 | | | | | | | | | Could not make specimens. |
| Bean IV-1 | 40 | 0.60 | 33 | 27 | 22 | 18 | 1.51 | 44 | 39 | 244 | Four specimens machined. |
| Bean V-2 | 40 | 1.00 | 47 | 36 | 32 | 24 | 1.45 | 36 | 31 | 150 | Four specimens machined |

*Modulus determined from tangent drawn to initial stress-strain curve.

1. e_b is the elongation at break and e_m is the elongation at maximum stress, both obtained by interpreting the crosshead travel relative to the stress-strain chart travel. M_{eb} is an approximate measurement of the actual elongation at break using a ruler and marks on the specimen's critical or "necked down" area. C_{em} is a calculated elongation at maximum stress based on e_m divided by e_b/M_{eb} . S_m is the maximum recorded stress and S_b is the stress recorded at specimen rupture. Mod is the modulus of elasticity calculated using S_m and C_{em} .

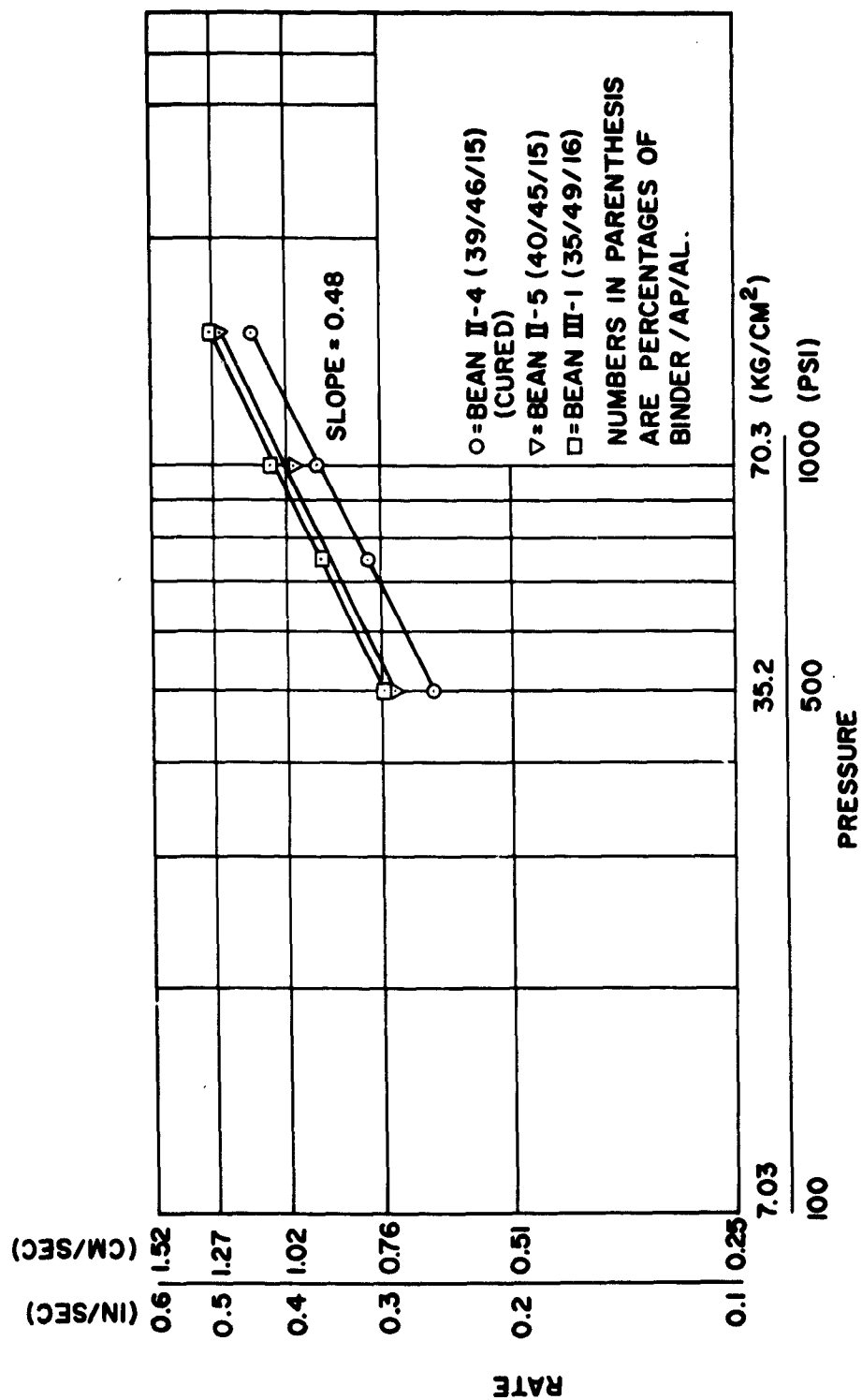


FIG.1 BURNING RATE VS PRESSURE

TABLE V
PROPELLANT CHARACTERISTICS

| Batch No. | % Binder | Carb./ epoxy ratio | Beansstalk contains ¹ | Burn Rate ² | | Density gm/cm ³ | Shore "A" Hardness Immed. | Impact Sens. 50% Hgt. (cm) | Vacuum Stability | |
|------------|----------|--------------------|----------------------------------|------------------------|---------------|----------------------------|---------------------------|----------------------------|------------------|-----------------------------------|
| | | | | temp | in/sec cm/sec | | | | 120°C | cc/gm, gas evolution 48 hr 168 hr |
| Bean I-1 | 30 | 0.75 | P+S | 19°C | .73 | 1.854 | | | | |
| Bean I-2 | 30 | 0.75 | P+S | 20°C | .56 | 1.422 | 79 | 59 | 30 | 0.9 |
| Bean II-1 | 40 | 0.75 | P+S | 21°C | .390 | 0.991 | | | | |
| Bean II-2 | 40 | 0.75 | P+S | 21°C | .39 | 0.991 | | | | |
| Bean II-3 | 40 | 0.75 | P+S | 21°C | .385 | 0.978 | | | | |
| Bean II-4 | 39 | 0.56 | P+S | 26°C | .360* | 0.914 | | | | |
| Bean II-5 | 40 | 0.75 | P+S | 25°C | .389 | 0.988 | | | | |
| Bean II-6 | 40 | 0.75 | P+T | | | 1.81 | 35 | 13 | | |
| Bean III-1 | 35 | 0.75 | P+S | 25°C | .417 | 1.059 | | | | |
| Bean III-2 | 35 | 0.75 | P+T | | | 1.86 | 45 | 19 | | |
| Bean IV-1 | 40 | 0.60 | P+T | | | 1.81 | 54 | 32 | 45 | |
| Bean V-2 | 40 | 1.00 | T | | | 1.82 | 43 | 26 | | |

*Propellant cured in soda straws (0.635 cm or 0.25 in I.D.)

- (1) P stands for Pentamer, S for S-Tricarboxylic acid, and T for T-Tricarboxylic acid.
(2) Burning rate is for uncured propellant burned in 0.635 cm I.D. soda straws, unless otherwise noted.

SECTION D. THEORETICAL BALLISTIC PROPERTIES

I. INTRODUCTION

Frozen and shifting specific impulses, I_{sf} and I_{ss} respectively, and volumetric impulse I_v , were computed for approximately one hundred propellant compositions based upon the BEANSTALK binder. Most of the calculations were done on the IBM 704 computer, utilizing programs developed by the Physical Chemistry Division of this Laboratory. The most recent calculations have used the Laboratory's IBM 7090 computer.

II. DISCUSSION

A. Binder System

Although many binder formulations have been under examination by the Laboratory, it was thought best for comparative theoretical impulse studies to employ a single binder throughout the calculations. The binder used has the formula $C_{2.4399}F_{0.2999}H_{3.2999}N_{0.9799}O_3$, and a calculated standard heat of formation* of -64.330 kcal/mol. Its theoretical maximum density is 1.55 g/cm³. Unless otherwise specified all the work reported here is based upon this binder. The data used for the binder, and the ingredients studied in combination with it, are shown in Table VI.

The results are presented in logical rather than chronological order, binary mixtures before ternary ones, regardless of the dates of calculation.

Figure II shows graphically volumetric impulse vs. density, for various values of I_{ss} . The points shown on the graph are discussed below. The area enclosed by the curve ABCD is the region of current practical interest- densities between 1.5 and 2 gms/cm³ and I_{ss} between 250 and 300 seconds.

*An exothermic reaction, by definition, gives a negative heat of formation.

B. Binary Mixtures

It had been expected that, in contrast to unoxygenated binders, this binder would have an optimum I_{ss}^* with a relatively low weight percentage of ammonium perchlorate; this was verified, and is shown in Figure III, where curves of I_{ss} vs wgt. % of binder are given for various oxidizers. The optimum I_{ss} of binder/AP mixtures is about 249.5 at the 40% binder level. This composition has an I_v of 441, Figure II.

Figure III also compares AP with some other potentially useful oxidizers, hydrazinium perchlorate (HP), nitronium perchlorate (NP) and hydrazinium nitroformate (HNF). Although the mixture binder/NP has, at maximum I_{ss} , the highest % of binder and therefore is easiest to process, the binder/HNF mixture gives the highest optimized I_{ss} .

C. Ternary Compositions

Figure IV is a tentative plot of I_{ss} vs % composition for the system binder/AP/Al. As the graph shows, the maximum I_{ss} obtainable is not unusual - slightly above 269. However, when densities of the compositions giving impulses of 266 and 268 were calculated, the corresponding volumetric impulses were about 511 and 485 grams force secs per cm^3 respectively. These are points 3 of Figure IV.

*All specific impulses quoted are calculated for a chamber pressure of 70.31 Kg/cm^2 (1000 psi) and an exit pressure of 1.03 Kg/cm^2 (14.7 psi).

TABLE VI
PROPELLANT INGREDIENT DATA

| <u>Symbol</u> | <u>Formula</u> | <u>ΔH_f^a</u> | <u>Density (gm/cc)</u> |
|-------------------------------------|--------------------------------------|----------------------------------|------------------------|
| Binder | $C_{2.44}F_{.29}H_{3.29}N_{0.98}O_3$ | -64.33 | 1.55 |
| Ammonium perchlorate (AP) | ClH_4NO_4 | -69.45 | 1.95 |
| Hydrazinium perchlorate (HP) | $ClH_5N_2O_4$ | -39.0 | 1.94 ^b |
| Nitronium perchlorate (NP) | $ClNO_6$ | + 8.0 | 2.25 |
| Hydrazinium nitro- formate (HNF) | $CH_5N_5O_6$ | -17.0 | 1.87 |
| Aluminum (Al) | Al | 0 | 2.71 |

/a In kcals/mol, H being positive for an endothermic reaction.

/b Schumacher, J.C. - Perchlorates, Their Properties, Manufacture and Uses.
Monograph. Am. Chem. Soc. (1939)

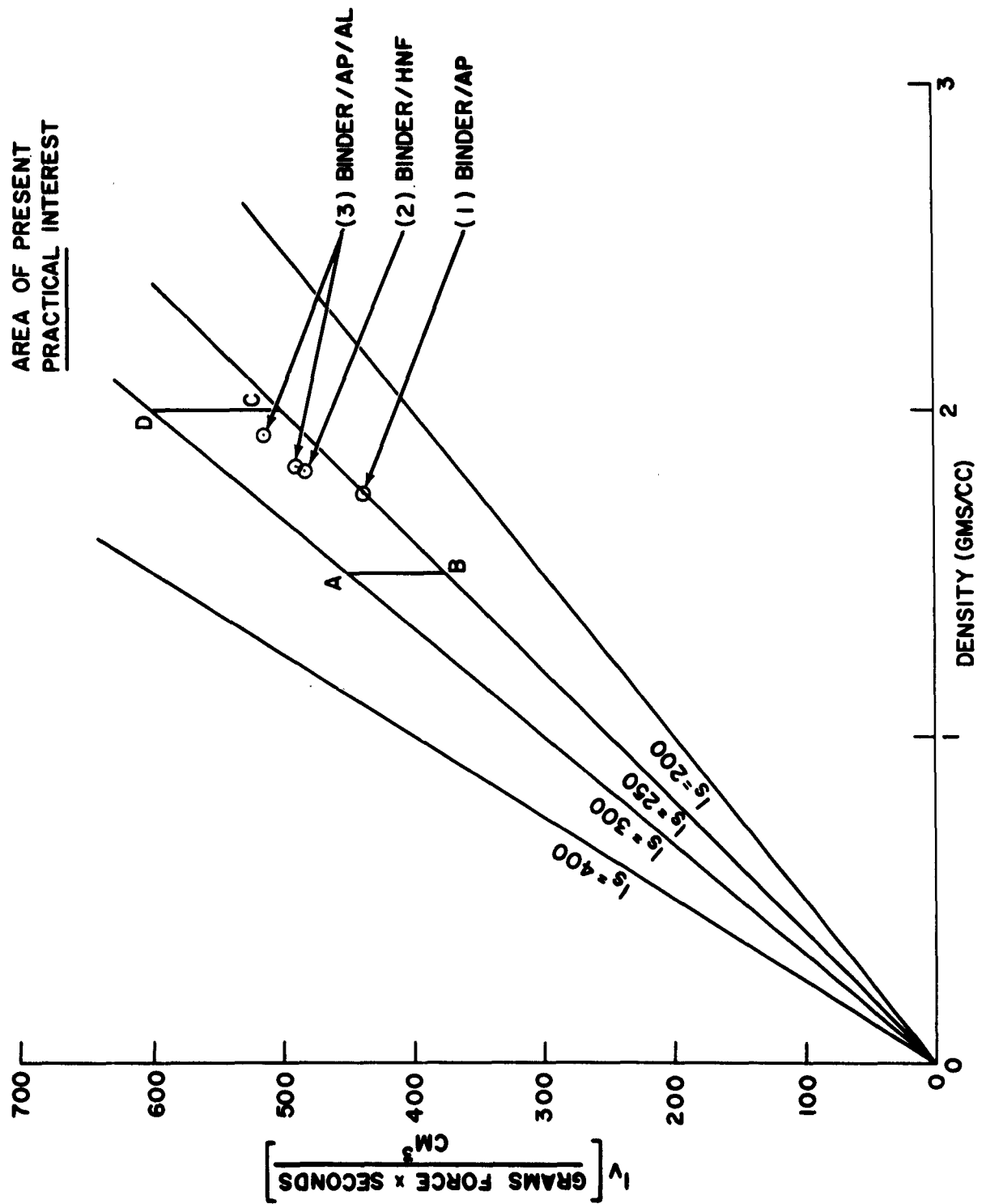


FIG. 2 VOLUMETRIC IMPULSE VS DENSITY FOR SEVERAL VALUES OF SPECIFIC IMPULSE

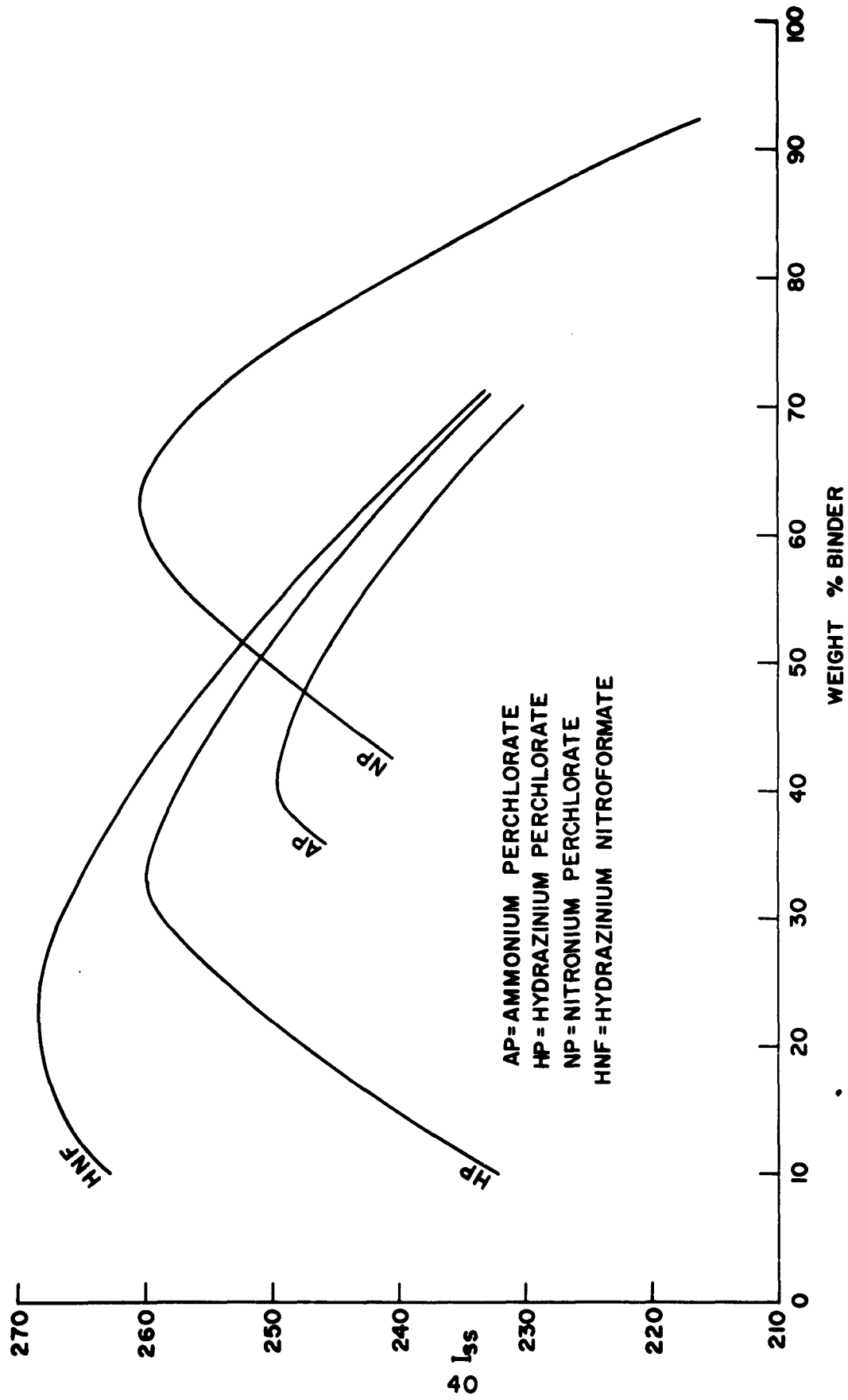


FIG. 3 SPECIFIC IMPULSE VS WEIGHT % BINDER

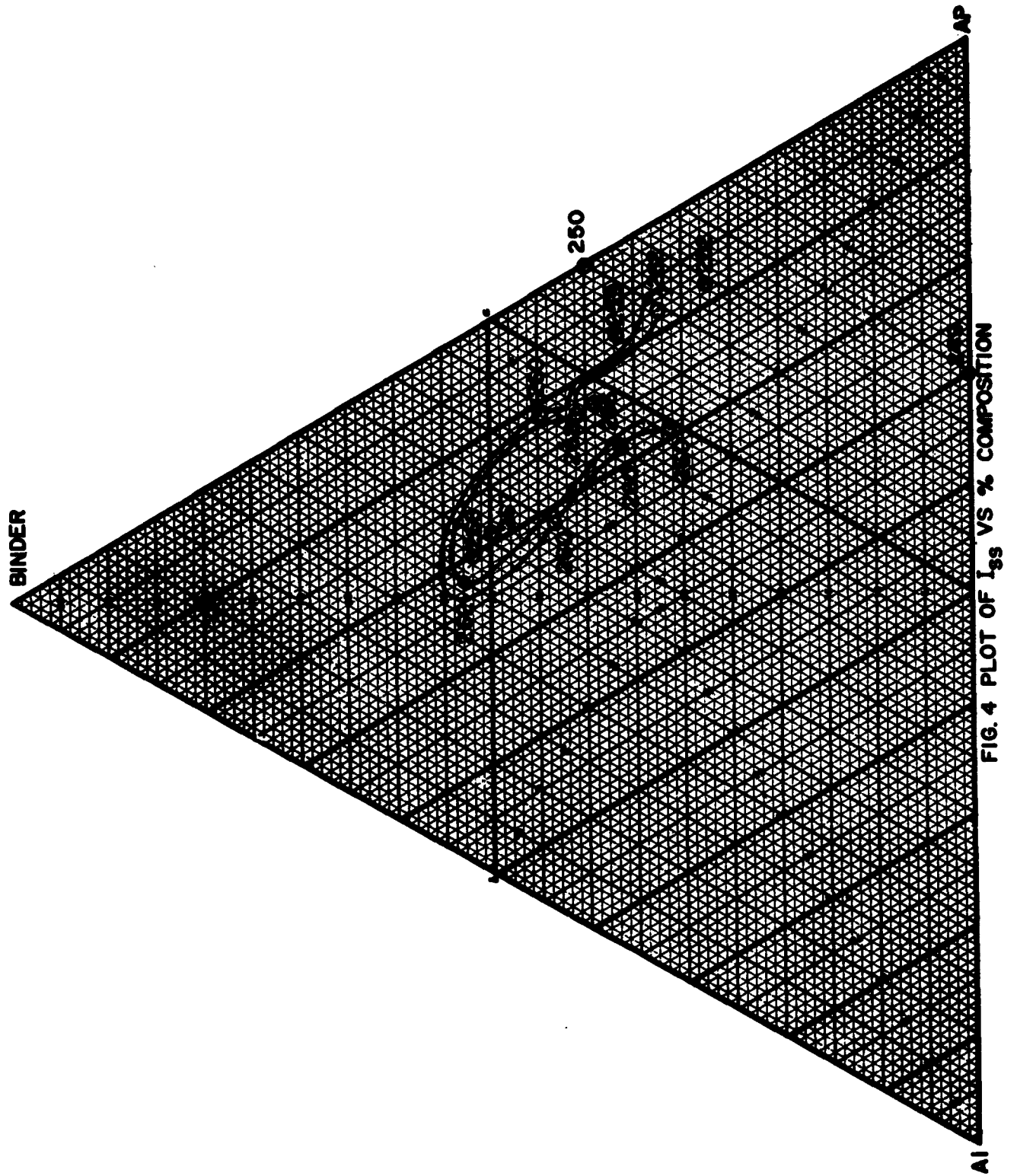


FIG. 4 PLOT OF I_{ss} VS % COMPOSITION

SECTION E. OVERALL SUMMATION

I. PROPELLANT PROPERTIES COMPARED TO TARGET VALUES

Table VII summarizes the progress on the Polaris Propellant Task. The data discussed below is for a propellant composition of binder/AP/Al (40/45/15). The propellant composition, binder/AP/Al (52/28/20), at maximum Isp should have about the same burning rate and better physical properties.

(a) Density - The density reported is 98 +% of theoretical maximum density and is above the target value.

(b) Thermal Stability - The thermal stability is excellent. It compares favorably with many propellants with non-energetic binders and is superior to any propellant with an energetic binder.

(c) Impact Sensitivity - The impact sensitivity is excellent. The binder is very insensitive. TNT pellets on the same scale are 150 cm as compared to 320 cm for the binder. While 45 cm for the propellant may not appear to be very insensitive when compared to 320 cm for the binder, it is in the same range as many composite propellants and less sensitive than double-base propellants which are in the 15-25 cm range.

In a recent test an attempt was made to detonate 4-one pound charges of the NOL propellant and 4-one pound charges of double base propellant. Two charges of each propellant were fired with 30 gm boosters and 2 with 100 gm boosters. All the double base charges detonated high order. None of the NOL propellant charges sustained a high order detonation. The two with 30 gm boosters deflagrated. The two with 100 gm boosters gave a more vigorous reaction which was not a steady state detonation.

These results seem to indicate that the propellant is relatively insensitive to shock. More gap tests with larger charges are needed to determine the effect of charge diameter on detonability.

(d) Tensile Strength - The strength is fair. Although we have not tested the latest propellant composition it is expected to be about 70 psi based on previous correlations between binder and propellant tensile strengths.

(e) Elongation - The elongation is low. Most of our efforts are concentrated on improving this property.

(f) Burning Rate - The burning rate has been consistently reduced. This has been accomplished by adjusting the particle size of the AP and Al. Since very little work in this area has been done, further reductions in burning rate are probable. The use of burning rate modifiers, which have not been tried, could lower the rate still further.

(g) Cure Time and Temperature - These properties have been improved to the point where they meet target values.

(h) I_{sp} - This is the theoretical calculated value. Since we are aiming for a delivered impulse of 260, this would require a theoretical I_{sp} of between 275-278 depending on combustion efficiency. It is unlikely that we can meet the target value with our present binder/AP/Al system. Several modifications of the original composition are being considered in an effort to increase the I_{sp}.

II. FUTURE PLANS

Our immediate need is to find ways and means to improve the physical properties of the binder. We will attempt to do this by synthesizing longer chain intermediates and prepolymers. We will also evaluate a number of new curing agents which have given experimental evidence of increasing both the strength and elongation of the binder.

A number of new prepolymers have been made. Propellants made from these prepolymers have a higher calculated I_{sp}, higher binder content and greatly improved physical properties. These propellants will be evaluated and the results presented in a later report.

TABLE VII
SUMMARY OF NOL PROPELLANT PROPERTIES

| Properties | Present Binder | Propellant | Target Propellant |
|--|-------------------|-----------------|----------------------|
| Density (measured) gm/cc lbs/in ³ | 1.50 0.0542 | 1.810 0.0654 | 1.80 0.0650 |
| Thermal Stability (cc/gm/48 hrs at 120°C) | -- | 0.9 | High |
| Impact Sensitivity (cm) | 320 | 45 | Low |
| Max. Tensile Strength (psi) Kg/cm ² | 67 4.7 | 70(a) 4.9 | 90-100 6.3-7.0 |
| Elongation at Max. Stress (%) | 104 | 25(a) | >60 |
| Burning Rate at 70.3/Kg/ cm ² (1000 psi) cm/sec in/sec | | 0.914 0.360 | 0.76 0.30 |
| Pressure Exponent | -- | 0.48 | -- |
| Cure Time (hrs) | -- | 72 | 48-72 |
| Cure Temperature (°C) | -- | 60 | 50-60 |
| Isp (Theoretical)(b) (lbf-sec/lbm at 1000 psia) | -- | 268 | 275-278 |

Propellant composition is AP/Al/Binder (45/15/40) except as noted.

- (a) Anticipated values based on present binder properties.
(b) Propellant composition is AP/Al/binder (28/20/52)

APPENDIX A
LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|--------------------------------------|---|
| Al | Aluminum |
| AP | Ammonium perchlorate |
| BDDO | Butadiene diepoxide |
| $[\text{BF}_3(\text{Et})_2\text{O}]$ | Boron trifluoride etherate complex |
| Ce_m | Calculated elongation at maximum stress based on e_m divided by e_b/Me_b |
| DNPA | 4,4-Dinitropimelic acid |
| DNVA | 4,4-Dinitrovaleric acid |
| e_b | % elongation at break as interpreted from crosshead travel |
| e_m | % elongation at maximum stress as interpreted from crosshead travel |
| FEFO | bis(2-2-dinitro-2-fluoroethyl)formal |
| Gly | Glycerol |
| H_f | Heat of formation |
| HNF | Hydrazinium nitroformate |
| HP | Hydrazinium perchlorate |
| I_{sf} | Frozen specific impulse |
| I_{ss}, I_{sp} | Shifting specific impulse |
| I_v | Volumetric impulse |
| Me_b | Actual elongation based on critical area |
| Mod | Modulus of elasticity calculated using S_m and Ce_m |

APPENDIX A(cont'd)

| | |
|----------------|-------------------------------------|
| NC | Nitrocellulose |
| N.E. | Neutralization equivalent |
| NP | Nitronium perchlorate |
| S _b | Stress recorded at specimen rupture |
| S _m | Maximum recorded stress |
| TEFO | bis(2,2,2-trinitroethyl)formal |
| VCDO | Vinylcyclohexene dioxide |

APPENDIX B

PREPARATION AND SCALE-UP OF BEANSTALK PREPOLYMERS

A. Scale-Up of Pentamer

No problems were encountered in scaling the 30-50 g preliminary Pentamer preparations to half-pound and eventually one-pound runs. A total of two half-pound and four one-pound preparations of Pentamer were carried out (see Table B-1) and the products supplied for polymerization studies. The esterifications were carried out under refluxing cyclohexane and the water of reaction was collected in a Dean-Stark trap. FEFO (53.3 wt. % in all cases) was added when the reactions were 60-70% to reduce viscosity during the final stages. Total reaction time was about 100 hours for all runs but the reaction mixture was stirred only when attended (generally about 30 hours). Water evolution (but not necessarily water formation) was more rapid when the reaction mixture was stirred indicating that, during the initial phases at least, diffusion of water from the reacting phase to the refluxing phase may have controlled the rate. About 75% of the theoretical amount of water was collected during the first 8 hours; eventual total water evolution ranged from 92.2 to 97.6%.

When the reactions were judged to be substantially complete the cyclohexane was removed first by heating to ca. 70-80° under water aspirator vacuum, then by holding for 2-3 days at ca. 75° under a vacuum of 0.5-2 mm. About 1% (ca. 2-5 g) of the polymer weight was generally recovered as FEFO in the dry ice trap after the latter operation.

The Pentamer, as thus prepared, was somewhat viscous at room temperature but easily pourable if first heated to 70°. Material balances were good and no significant decomposition was observed during the reaction or in the course of the drying procedures. Agreement between extent of esterification as measured by water evolved and as measured by neutralization equivalent¹³ was fair.

In one run the material recovered in the dry ice trap was identified as fluorodinitroethanol rather than FEFO. It is believed that the fluorodinitroethanol was an impurity in that particular batch of Aerojet FEFO rather than a by-product of the reaction.

B. Preparation of One Pound Batch of Pentamer

Through one neck of a 2 liter-3 neck flask equipped with a thermometer, mechanical stirrer and Dean-Stark trap (Note 1) surmounted by a reflux condenser were added 38.38 g. (0.4005 mole) glycerol, 76.94 g (0.4005 mole) 4,4-dinitrovaleric acid and 150.28 g.(0.6007 mole) 4,4-dinitropimelic acid (Note 2). Approximately 500 ml of cyclohexane was added and the mixture heated with stirring until the lower phases fused into a white doughy mass. After cooling to 60°, 0.80 g. p-toluenesulfonic acid monohydrate was added and the mixture heated to reflux and stirred. Water was removed by azeotropic distillation (Note 3). When 63% of the theoretical amount of water had been collected the mixture was cooled to 50-60° and 276.26 g. FEFO was added. The mixture was again heated to reflux. It was refluxed with stirring for a total of three and one-half 8 hour days and without stirring for three 16 hour nights and a 72 hour weekend for a total of 124 hours. About 70% of the water was evolved during the first 6 hours; stirring and heating were discontinued after 97.6% of the theoretical amount of water had been collected.

(Note 1) A 15 ml Dean-Stark trap was used and interchanged with a second trap of 10 ml capacity after about 14 ml of water had been collected. To get a good meniscus reading it is essential that the traps be cleaned as thoroughly as possible. The traps were cleaned with freshly prepared sulfuric acid-dichromate solution (4 g. potassium dichromate, 10 ml water and 130 ml concentrated sulfuric acid) by heating on the steam bath for 1-4 hours, rinsing thoroughly (at least ten times) with water and several more times with distilled water. The traps were dried 1-2 hours in the oven prior to use.

(Note 2) Glycerol, on account of its viscosity, is quite difficult to measure quantitatively. For this reason the glycerol was first added to the flask and weighed by difference and the amounts of the other components adjusted to that of the glycerol. The glycerol contained ca. 4% water and this was taken into account in calculating extents of reaction from water evolved.

(Note 3) The theoretical amount of water is computed from three sources: (1) water of reaction, (2) water from the glycerol, (3) catalyst water. The theoretical amount in this case was calculated to be 23.25 ml.

Removal of most of the cyclohexane was effected by water aspirator vacuum distillation, the pot temperature being eventually raised to 75-80°. Final traces of low-boilers were removed by holding the product at 78-80°C and 0.50-2.0 mm for a period of three days (shorter periods may be equally effective).

The amber-brown prepolymer was then drained into a tared flask while still at 75-80°. Drainage during the last stages was quite slow and it was convenient to clamp the flask in an inverted position. To remove as much material as possible the flask was reheated a number of times. A total of 505.3 g. of prepolymer was collected and it was determined by weighing, washing thoroughly with acetone and reweighing that an additional 10.1 g. had still adhered to the flask. The total amount recovered was 515.4 g. as compared to the theoretical amount of 518.6 g. Part of the difference was accounted for by 1.2 g. FEFO collected in the dry-ice trap in the line leading to the vacuum pump.

C. Scale-Up of S-Tricarboxylic Acid

Two small scale preparations of S-Tricarboxylic acid containing 33.6 and 52.6% respectively of FEFO were carried out without major difficulty (see Table B-2). Water evolution was 87% in the one case, 93% in the other and material balances were good. No significant evidence of decomposition was observed; only traces of FEFO were found in the dry ice trap after the prolonged drying operation. The products were more viscous at both ambient and elevated temperatures than Pentamer but were, nevertheless, pourable if heated.

When an attempt was made to repeat these reactions on a one-pound scale serious difficulties were encountered. During the fourth night of reaction when ca. 93% of the theoretical amount of water had been collected, the unstirred mixture apparently gelled. The gel could not be broken by stirring or by further addition of FEFO. Copious amounts of hot acetone did partially break the gel and an attempt was made to recover a usable product by distilling off the acetone. The product thus obtained, however, was inhomogeneous and gave inhomogeneous mixtures with Pentamer and was consequently discarded. This experience forced a search for other tricarboxylic acids. Whether the gelation was due to chemical or physical phenomena (e.g. emulsification) has become a moot point since the alternative tricarboxylic acids fortunately showed enhanced properties in a number of respects and would have been preferred even had the gelation not been observed with the S-acid.

D. Scale-Up of T- and TF-Tricarboxylic Acids

Three preparations of T-Tricarboxylic acid and two of TF-Tricarboxylic acid were carried out (see Tables B-3 and B-4). In neither instance were difficulties observed in scaling up to one-pound batches. Water collected ranged from 94-99% and material balances in all cases were good. The products were about as viscous as S-Tricarboxylic acid at ambient temperatures but somewhat less viscous at elevated temperatures. The T-Tricarboxylic acids as supplied contained 50% FEFO, the TF-Tricarboxylic acids 40% FEFO. No significant amounts of FEFO were collected in the dry ice trap during the drying.

E. Preparation of a One-Pound Batch of T-Tricarboxylic Acid

Substantially the same procedure was used as in the preparation of Pentamer. Reactants were 38.34 g. (0.400 mole) glycerol, 200.13 g. (0.800 mole) dinitropimelic acid and 38.43 g. (0.200 mole) dinitrovaleric acid together with 500 ml cyclohexane, 0.80 g. p-toluenesulfonic acid monohydrate and 253.65 g. FEFO. FEFO was added when 50% of the theoretical amount of water had been collected. Total reflux time was 107 hours, of which 43 hours was with scirring. Total water collected was 96.8% of theoretical.

The amount of T-Tricarboxylic acid collected was 490.7 g. and it was determined that 13.7 g. had adhered to the flask. The total of 504. g. recovered compared with 507.3 g. theoretical. Only traces of FEFO were found in the dry ice trap.

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TABLE B-1

LARGE SCALE PENTAMER PREPARATIONS

| | B A T C H | | | | | |
|---|-----------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Reactants, moles | | | | | | |
| DNVA | 0.200 | 0.400 | 0.203 | 0.404 | 0.400 | 0.400 |
| DNPA | 0.300 | 0.600 | 0.304 | 0.606 | 0.600 | 0.600 |
| Gly | 0.200 | 0.400 | 0.203 | 0.404 | 0.400 | 0.400 |
| FEFO Wt. % | 52.3 | 53.3 | 53.3 | 53.3 | 53.3 | 53.3 |
| H ₂ O Collected % of Theoret. | 92.2 | 96.1 | 96.0 | 92.0 | 96.2 | 97.6 |
| Prepolymer Materials | | | | | | |
| Balance, g. | | | | | | |
| Obtained | 257.2 | 511.8 | 261.0 | 525.6 | 513.6 | 515.4 |
| Theoret. | 259.2 | 518.4 | 262.7 | 526.1 | 518.6 | 518.6 |
| Neutral Equiv. (14) | | | | | | |
| Theoret. | 1295 | 1295 | 1295 | 1295 | 1295 | 1295 |
| Found | 1054 | 1190 | 1048 | 1066 | 1089 | 1124 |

Comments:

- Run 1. Product was clear, pale chartreuse liquid.
 Run 2. Reddish amber, recovered 3.34 g. $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OH}$ in dry ice trap.
 Run 3. Reddish brown.
 Run 4. Deep amber. Less viscous than previous batches.
 Run 5. FEFO from Aerojet was slightly yellow.
 Run 6. Brownish material.

TABLE B-2

S-TRICARBOXYLIC ACID PREPARATIONS

| | B A T C H | | |
|---|-----------|-------|-------|
| | 1 | 2 | 3 |
| Reactants, moles | | | |
| DNPA | 0.120 | 0.245 | 0.943 |
| Gly | 0.040 | 0.082 | 0.314 |
| FEFO, Wt. % | 52.6 | 33.6 | 55.0 |
| H ₂ O Collected % of Theoret. | 87.1 | 93.0 | 93.8 |
| Prepolymer Materials | | | |
| Balance, g. | | | |
| Obtained | 63.4 | 96.6 | 528.0 |
| Theoret. | 66.3 | 96.9 | 551.0 |
| Neutral Equiv. (14) | | | |
| Theoret. | 553 | 395 | 584 |
| Found | 501 | 377 | 563 |

Comments:

- Run 1. Product was light brown and thick, pourable at 80°C.
 Run 2. Viscous brownish oil.
 Run 3. Suspect run. Material formed a gel that was broken only after much effort.

TABLE B-3

T-TRICARBOXYLIC ACID PREPARATIONS

| | B A T C H | | |
|---|-----------|-------|-------|
| | 1 | 2 | 3 |
| Reactants, moles | | | |
| DNVA | 0.020 | 0.100 | 0.200 |
| DNPA | 0.080 | 0.400 | 0.800 |
| Gly | 0.040 | 0.200 | 0.400 |
| FEFO Wgt. % | 50.9 | 50.0 | 50.0 |
| H ₂ O Collected % of Theoret. | 100 | 93.8 | 96.8 |
| Prepolymer Materials | | | |
| Balance, g. | | | |
| Obtained | 49.5 | 254.5 | 504.4 |
| Theoret. | 51.0 | 255.5 | 507.3 |
| Neutral Equiv. (14) | | | |
| Theoret. | 845 | 845 | 845 |
| Found | 788 | 781 | 752 |

Comments:

- Run 1. Viscous amber liquid. Probably obtained some water of condensation in reaction.
Run 2. Brownish viscous material, easily pourable at 70-80°C.
Run 3. Amber liquid.

TABLE B-4

TF-TRICARBOXYLIC ACID PREPARATIONS

| | B A T C H | |
|----------------------------|-----------|-------|
| | 1 | 2 |
| Reactants, moles | | |
| DNFBA | 0.050 | 0.200 |
| DNPA | 0.202 | 0.800 |
| Gly | 0.101 | 0.400 |
| H ₂ O Collected | 96.4 | 99.0 |
| % ² of Theoret. | | |
| Prepolymer Materials | | |
| Balance, g. | | |
| Obtained | 107.8 | 424.7 |
| Theoret. | 107.3 | 425.0 |
| Neutral Equiv. (14) | | |
| Theoret. | 707 | -- |
| Found | 653 | -- |

Comments:

Run 1. Brown viscous liquid, pourable at 70-80°C.

Run 2. Brown viscous liquid, pourable at 70-80°C.

Both batches contained 40 wt. % FEFO.

APPENDIX C

PROCEDURE FOR EVALUATION OF BEANSTALK PREPOLYMER BATCHES

Table C-1 shows a number of measured and calculated values for the various prepolymers.

The following assumptions were made:

- (1) The prepolymer solution is perfectly homogeneous.
- (2) No component of the solution is volatile. No material is lost during solvent removal.
- (3) Water formed during the esterification reaction is removed completely.

The neutralization equivalent was obtained by titration of the prepolymer solution in acetone with a standard NaOH solution. Thymol blue was used as the indicator.

A graph was first made of the neutralization equivalent of the prepolymer solution as a function of the % complete reaction.

$$\text{N.E. (Solution)} = \frac{A + B + C(1-R)}{n + m(1-R)}$$

where N.E. = neutralization equivalent

A = molecular weight of polymer if 100% reacted

B = weight of FEFO

C = weight of water removed if 100% reacted

n = functionality of polymer if 100% reacted

m = number of moles of water removed if 100% reacted

R = fraction of total reaction (%/100)

The measured neutralization equivalent was used to find the % reaction on this graph. The % reaction was then used to find the other values.

$$\text{N.E. (Polymer)} = \frac{A + C(1-R)}{n + m(1-R)}$$

$$\text{M.W. (Polymer)} = \frac{A + C(1-R)}{1 + m(1-R)}$$

$$\text{Functionality} = \frac{\text{M.W. (Polymer)}}{\text{N.E. (Polymer)}}$$

These calculations might have a more accurate base if the hydroxy equivalent of the polymer had been determined as well as the neutralization equivalent. A check on the % reaction could be made by using the hydroxy equivalent.

TABLE C-1
EVALUATION OF PREPOLYMER BATCHES

| Polymer Type | Batch No. | % FERO in Prepolymer | N.E. Measured | % Complete Reaction | N.E. Polymer | Avg. Mol.Wt. | Functionality |
|----------------------|-----------|----------------------|---------------|---------------------|--------------|--------------|---------------|
| Pentamer | -- | 53.3 | 1295 | 100.0 | 605 | 1210 | 2.00 |
| | 1 | " | 1054 | 92.2 | 494 | 830 | 1.68 |
| | 2 | " | 1190 | 97.1 | 558 | 1033 | 1.85 |
| | 3 | " | 1048 | 92.0 | 491 | 823 | 1.68 |
| | 4 | " | 1066 | 92.7 | 500 | 847 | 1.69 |
| | 5 | " | 1089 | 93.6 | 510 | 879 | 1.72 |
| | 6 | " | 1124 | 95.0 | 528 | 935 | 1.77 |
| | 5 + 6 | " | 1106 | 94.2 | 518 | 902 | 1.74 |
| S-Tricarboxylic acid | -- | -- | -- | 100.0 | 263 | 788 | 3.00 |
| | 1 | 52.5 | 501 | 89.0 | 238 | 597 | 2.51 |
| | 2 | 33.5 | 377 | 95.0 | 251 | 688 | 2.74 |
| | 3 | 55.0 | 563 | 96.0 | 253 | 706 | 2.79 |
| T-Tricarboxylic acid | -- | 50.0 | 845 | 100.0 | 423 | 1268 | 3.00 |
| | 1 | " | 788 | 96.5 | 396 | 1051 | 2.65 |
| | 2 | " | 781 | 95.8 | 391 | 1016 | 2.60 |
| | 3 | " | 752 | 93.7 | 377 | 925 | 2.45 |

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| | DESCRIPTORS | CODES | DESCRIPTORS | CODES |
|-------------|-------------|-------|---------------|-------|
| Energetic | | ENER | Glycerol | GLYR |
| Binders | | BIND | Plasticized | PLSZ |
| Solid | | SOLI | Ris | RISE |
| Propellants | | FUEL | Fluoro | FUOR |
| Ammonium | | AMON | Dinitro | DINT |
| Perchlorate | | PERH | Ethyl | ETHL |
| Aluminum | | ALUM | Formal | FORL |
| Carboxy | | CABY | Thermal | THER |
| Nitro | | NITR | Stability | STBL |
| Polyesters | | POLR | Insensitivity | INSN |
| Synthesia | | SYNS | Impact | IMPC |
| Acids | | ACID | Shock | SHOC |
| | | | Values | VALU |
| | | | Tensile | TENS |
| | | | Strength | STEN |
| | | | Elongation | ELON |
| | | | Burning rate | BURR |
| | | | Burning | BURN |

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